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भारत सरकार

GOVERNMENT OF INDIA

परमाणु ऊर्जा आयोग

ATOMIC ENERGY COMMISSION

ANNUAL REPORT OF THE METALLURGY DIVISION

Period Ending December 1977

Edited by

K. Elayaperumal, Ch. Sridhar Rao, P. Mukhopadhyay and S. V. K. Rao

Metallurgy Division

भाभा परमाणु अनुसंधान केन्द्र

BHABHA ATOMIC RESEARCH CENTRE

बंबई, भारत

BOMBAY, INDIA

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ZIRCONIUM OXIDES

CORROSION

NIOBIUM

VANADIUM

NICKEL

TITANIUM

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BHABHA ATOMIC RESEARCH CENTRE
METALLURGY DIVISION

1. Summary Progress Report for 1975-77

The Metallurgy Division is engaged in a wide variety of programmes dealing with special materials development for nuclear, space and electronic applications, and the elucidation of materials behaviour in engineering systems. The programmes cover extraction metallurgy, physical & mechanical metallurgy, alloy development, corrosion metallurgy, and ceramics, including property evaluation of both metallic and ceramic materials. The three year period 1975-77 has seen substantial progress in all these fields. The following are some of the highlights of major achievements :

Process Development & Pilot Plants

1. Work is in progress to set up a Beryllium Pilot Plant at Vashi, with an initial annual capacity of 10 tonnes of Cu-2%Be alloy and 250 Kg of vacuum hot pressed beryllium metal. The project is in collaboration with the Departments of Space and Electronics.

2. Regular production of boron carbide and boral sheet has been undertaken for meeting the requirements of reactor programmes. Ring-shaped boron carbide - aluminium composites have also been successfully fabricated.

3. In the Titanium Pilot Plant programme, fluidised bed chlorination of rutile to produce $TiCl_4$ at a rate of about 20 Kg/hour, and fused salt electrolysis of $TiCl_4$ in a refractory-lined 1000 amp electrolytic cell have been successfully demonstrated.

4. Process flowsheets have been developed for (i) recovering nickel and molybdenum values from the sulphide concentrates of UCIL, (ii) preparing vanadium-base materials from the by-products of the aluminium industry, (iii) fabricating Nb-Ti superconductors, and (iv) re-processing of zirconium scrap.

5. A method has been developed for graphite coating of zircaloy fuel tubes to minimise pellet-clad interaction in power reactor fuels.

6. A technique for hard wear resistant chromium plating has been developed to meet some of the requirements of R-5. The wear resistance is required in the metallic seals of the lattice tubes. It is proposed to plate the entire metallic seals of R-5.

7. In a programme on the development of plate type fuel elements made of high density, thin, sintered platelets of UO_2 and UO_2-ZrO_2, the powder preparation and fabricational parameters have been optimised.

8. In the field of high temperature ceramic materials for the MHD channels, sintered high density bodies of Al_2O_3 and MgO with optimum porosity have been successfully developed based on admixtures of fused and active oxides which would withstand the severe service conditions in the MHD channels.

New Equipment Facilities

1. A Scanning Electron Microscope has been installed and is being extensively used for studies on failure analysis of components from various units of DAE and for characterisation of fine metal powders.

2. A new Transmission Electron Microscope has been installed and is being used for studying phase transformations and other structural aspects in zirconium-base alloys and other nuclear materials.

3. A freeze-drying unit has been designed and commissioned for the preparation of ultra fine particles of metal compounds for further conversion to fine metal powders required in the preparation of porous metal components of controlled porosity.

4. A 5-litre high pressure high temperature autoclave has been fabricated. Using this autoclave stress corrosion cracking of (i) zircaloy-2 fuel tube in iodine vapour, and (ii) steam generator tube materials like inconel, monel and incoloy in high temperature water have been established.

5. In collaboration with Desalination & Effluent Engineering Division, a dynamic corrosion loop has been set-up to study corrosion behaviour of Desalination Plant materials both in raw sea water and under various desalination conditions.

Basic Research

In addition to the above listed developmental programmes, the Division has made very valuable contributions of fundamental significance in several branches of Materials Science. The specific fields include : metallurgical thermochemistry; gas-solid reactions; physical, mechanical and structural properties of cladding and pressure vessel materials; metal. physics aspects like diffusion and radiation damage; stress corrosion cracking; passivity, pitting and other electrochemical characteristics of corrosion of metals; electroplating of alloys and composites and characterisation of ceramic powders and mechanism of sintering.

Consultancy and Technical Services

The Division continues to extend Consultancy and Technical Services to several organisations both within and outside DAE, in the form of supply of special materials assistance in carrying out materials evaluation tests, advice on materials selection and participation in failure analysis investigations.

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The major applied research programmes in the Metallurgy Division have been concerned with (i) development of processes for the extraction and refining of strategic metals and special materials of interest to nuclear engineering, electronics, aero-space, and chemical industries, (ii) studies on the physical, mechanical and corrosion properties of these materials, (iii) development of high temperature ceramic materials for advanced applications as in the MHD programme and (iv) development of special fabrication techniques, involving powder metallurgy and electroforming. Basic research programmes currently in progress are in the areas of metallurgical thermochemistry, diffusion, structural metallurgy, radiation damage, corrosion kinetics and sintering. The Division has also been extending assistance to several organisations, meeting their specific material requirements, and participating in investigations on materials performance and failure analysis.

The setting up of a Beryllium Pilot Plant (Initial Annual Capacity: 10 tonnes of Cu-2% Be and 250 Kg vacuum hot pressed beryllium metal) - in collaboration with the Department of Space and Department of Electronics - has been approved. There has been good progress on the development of graphite-coating of zircaloy tubes, to minimise pellet-clad interaction in power reactor fuel. Ring-shaped boron carbide-aluminium composites have been successfully fabricated for use as control rod material. Attractive pyro- and hydro-processing schemes have been evolved to recover nickel and molybdenum values from the sulphide concentrates in the by-product recovery plant of UCIL. Process flowsheets for the recovery of vanadium in diverse industrially important usable forms, such as pure

vanadium, ferro-vanadium and vanadium oxycarbide have been developed, starting from by-products of the aluminium industry and also from vanadiferous slag. A plasma furnace facility is being set up for investigating new extractive processes at high temperatures. Molten salt electro-winning and electro-refining processes have been continued to produce ductile titanium and hafnium, and for the reclamation of zircaloy scrap.

Extensive work has been carried out on phase transformations, structure-property correlations, solid state diffusion and radiation damage. These studies include: the martensitic transformation and the precipitation of metastable and stable intermetallic phases in the binary Zr-Al, Zr-Cu, Zr-Cr, Zr-Ta, Zr-Sn, Zr-Nb, Ti-Cr and Ti-Mo systems; rationalisation of the observations in terms of computer-generated free energy varous composition data; the influence of the second phase on the strength properties of these alloys; the effects of a variety of heat treatments on the microstructure and the mechanical properties of important structural alloys like zircaloy-2, Zr-2.5Nb, Ti-6Al-4V, Ti-8Al-1Mo-1V and Ti-6Al-2Sn-4Zr-6Mo; establishment of a detailed structure-property correlation in the reactor pressure vessel steel HY-130; diffusion behaviour in the Zr-Fe, Ti-Fe, Th-Fe and Zr-Cr systems; the mechanisms of solid solution hardening in a number of zirconium alloys; microstructural characterisation of some important superconducting alloys and compounds; the effect of neutron irradiation on the mechanical properties of some titanium alloys; ion-irradiation induced blister formation on several nuclear structural materials; and setting up of a versatile gas pressure bonding assembly for studying the diffusion bonding behaviour of zircaloy-2. Apart from these research programmes, the Division has provided service facilities to external users, for transmission and scanning electron microscopy, electron probe micro-analysis, and Instron testing.

Studies on the high temperature corrosion of zircaloy-2

containing aluminium as impurity have shown that aluminium contents up to 140 ppm can be tolerated from the view-point of acceptable corrosion rates. In the high temperature corrosion of carbon steel in lithiated water at an oxygen level of 0.05 ppm, the corrosion product release rates have been observed to be extremely low. High temperature autoclave collapse tests for ridging on RAPP fuel pins have indicated that low yield strength fuel-clad may be accepted provided the pellet-clad gap is less than 0.003 inch. Studies on stress corrosion cracking (SCC) of zircaloy-2 in iodine have shown that annealed tubes are susceptible to SCC by iodine during internal pressurisation. As regards the effects of alloying elements on the stress corrosion cracking of zirconium, it has been observed that iron and copper are not as effective as chromium in imparting resistance. Nickel, both in the wrought and electrodeposited form, has been found to be resistent to corrosion in highly alkaline solution, but this resistance is affected by impurities in the alkaline solution, particularly H_2S. Studies on sea water corrosion in CIRUS jetty have shown that a copper base alloy Cu-9%Sn-4%Al is resistant to sea water. Electroplating of antimony, Ni-Mn alloys, Ni-TiO_2 composites, electrophoretic deposition of NiO, electroforming of porous nickel tubes, and particle-bed electrolysis of dilute copper solutions have been successfully carried out in the Electrometallurgy programmes.

In the field of nuclear ceramics, R & D studies are being carried out on UO_2, UO_2-ZrO_2 and BeO. A programme on the development of high-density, thin sintered platelets of UO_2 and UO_2-ZrO_2 has been taken up. For the plate-type fuel development, the powder preparation and fabricational parameters have been successfully optimised. In the field of high temperature materials, for the development of high-temperature oxide ceramics for the MHD channels, R & D studies are being carried out on Al_2O_3, MgO and ZrO_2. Sintered high density bodies of Al_2O_3 and MgO with optimum porosity have been successfully developed based on admixtures of fused and active oxides which would withstand the severe service conditions in the MHD channels. Work

has also been initiated on rare-earth stabilised zirconia for use as the hot electrodes in these channels. In the field of electrical ceramics, in addition to the R & D studies on Barium Titanate capacitor and Ni-Zn Ferrite bodies, work has been taken up to develop high density impervious high alumina components to very close dimensional tolerances - of great importance to the electronics industry.

(C. V. Sundaram)
Head, Metallurgy Division

2. EXTRACTIVE METALLURGY

The major activities of the Section were concerned with studies on (i) the treatment of ores, concentrates and industrial by-products for the recovery of strategic metal values, (ii) the extraction and refining of rare, reactive and refractory metals for engineering application, (iii) preparation and fabrication of special materials for control-rod, superconducting and magnet applications, (iv) metallurgical thermo-chemistry, (v) development of high temperature furnaces, plasma processes, and (vi) fluidised bed reactors. Special emphasis was placed on the development of processes for the extraction of niobium, vanadium, hafnium, the rare earth metals and nickel, preparation of niobium alloys, rare earth alloys, boron carbide and composites; and generation of process data and equipment design. High temperature reactions were studied to obtain thermodynamic and kinetic data. Regular production of boral sheets, boron carbide, ferro alloys and other special alloys was continued.

2.1 BORON CARBIDE AND BORAL SHEETS

2.1.1 Boral Sheets

(C.K. Gupta, D.K. Bose, T.K. Mukherjee and K.U. Nair)

Regular production of boron carbide (B_4C) by carbothermic reduction of B_2O_3 with carbon/coke in a 30 KW induction furnace was carried out. The product carbide is being used for preparing the boral sheets for supplying to the R-5 project.

The process standardised for the fabrication of boral sheets involved three main steps, namely (i) production of boral block, (ii) picture framing of the boral block with aluminium and (iii) hot rolling to clad-sheet.

Boral blocks (200 x 150 x 20 mm) containing 35%(wt)B_4C, dispersed in aluminium matrix were prepared by hot pressing B_4C (pre-oxidised) and aluminium powder mixture in a graphite die at 700°C and 1-3 kg/cm^2 pressure. The blocks were placed inside a 6 mm thick aluminium picture frame and jacketted with a 3 mm thick aluminium plate. Vent holes (3 mm ø) were also provided in the frame. The blocks thus

encased all around with aluminium were heated to 600/610°C, soaked for half an hour and hot rolled, giving 10% reduction per pass. On the average, 9 to 10 passes were possible between successive heating cycles. The sheets were rolled to a final thickness of 10 mm and then cut to 200 x 300 mm sizes, as specified.

2.1.2 Large Scale Production of B_4C

(C.K. Gupta, B.R. Mahendra, P.V.S. Pillai, C. Narayanan and K.U. Nair)

In order to produce boron carbide on a large scale, a direct electric resistance heating furnace assembly was built and successfully tested. The furnace consisted of a graphite heating element (25 dia x 5 th x 150 mm long) placed vertically between two water cooled graphite terminals. The element was assembled in a graphite crucible, which contained the charge, B_2O_3 and coke. An 80 KW single phase transformer was used to supply the power and heat the element and the charge to the reduction temperature of more than 2000°C. With 12 KW power input reduction was continued for 2 hours to obtain dense boron carbide crystals. Further work is in progress on increasing the batch size, and to establish the operating parameters.

2.2 NIOBIUM AND ITS ALLOYS

2.2.1 Niobium through Niobium Nitride Route

(S.P. Garg, N. Krishnamoorthy and R. Venkatramani)

An alternative process, to the aluminothermic and carbothermic reductions for the preparation of niobium was investigated. The process involved nitriding of Nb_2O_5 in presence of carbon under nitrogen atmosphere followed by denitriding under vacuum and electron beam melting / refining of the metal :

$$Nb_2O_5 + 5C + N_2 \longrightarrow 2\ NbN + 5\ CO$$

$$2\ NbN \longrightarrow 2\ Nb + N_2$$

Pellets of niobium oxide and graphite mixture (100 gm) were placed in a molybdenum lined graphite crucible and heated in an induction furnace at 1500°C for 2 hours under flowing (500 cc/min) nitrogen. Nitrogen flow was then stopped; the temperature was raised under dynamic vacuum of 10^{-3} torr and denitriding was carried out for one hour at 1950°C. The metal thus obtained was found to be 99.5% pure (130 VPN). Further purification could be achieved by electron beam melt-refining and the final product corresponded to a button hardness of 70 VPN.

2.2.2 Niobium by Aluminothermic Reduction

(C.K. Gupta and C. Narayanan)

Over 5 kg of niobium metal was prepared by the aluminothermic reduction of Nb_2O_5 followed by electron beam melting. The high purity metal is being used in the development programme on Nb-Ti superconducting alloy.

2.2.3 Niobium-titanium Alloy

(C.K. Gupta, D.K. Bose and C. Narayanan)

In the programme on super-conducting Nb-Ti alloys, alloys with higher Ti content were prepared. Various steps in the fabrication of copper-clad Nb-Ti wire were standardised. Long length, OFHC copper-clad wires of 0.3 mm dia and 25 metres long were prepared. A typical wire containing Nb-25Ti was found to carry 2×10^5 Amp/cm^2 upto a field of 40 kg. In order to increase the current carrying capacity (upto 1×10^6 amp/cm^2) of such wires, alloys with 55-60 wt%Ti were prepared. These alloys were amenable to cold rolling to the extent of 60% reduction without intermediate annealing. Short sample tests on these wires are being carried out at the RRC, Kalpakkam.

2.3 ZIRCONIUM

2.3.1 Electro-refining of Zircaloy Scrap

(J.C. Sehra, P.L. Vijay and A. Unnikrishnan)

In order to develop an alternative process for reclamation

of zircaloy scrap, studies on electro-refining technique were continued. The scrap was obtained from the Nuclear Fuel Complex, for the investigations on 1 kg scale. Under the optimum operating conditions established, dendrititic deposit of good quality metal was obtained. The overall metal yield and the current efficiencies were found to be about 65% and 75-80% respectively. The electro-refined and arc melted zirconium metal corresponded to a button hardness of 150 VPN.

Based on these studies, a large scale unit has been designed and is being fabricated at the Central Workshops, BARC.

2.3.2 Al-Zr Master Alloys

(T.S. Krishnan, R.P. Tangri and P.K. Rajagopalan)

Zirconium is added as a grain-refiner to aluminium, to improve the mechanical properties. The estimated demand for Al-5%Zr master alloy for this application is of the order of 150 tons in the defence industry alone. An enquiry for the supply of 2 tonnes of Al-5%Zr alloy has been received from M/s Indian Aluminium Company, Calcutta.

Two processes, one based on direct alloying and the other on aluminothermic reduction of ZrO_2 in presence of cryolite for the preparation of Al-5-15%Zr master alloys were established on the bench scale. Based on the results of direct alloying, large scale melts (25-30 kg) making use of the facilities at Central Workshops have been planned.

2.3.3 Ferro-zirconium

(D.K. Bose and O.K. Mehra)

Ferro-zirconium finds application as an alloying agent and also as a de-oxidiser in the steel industry. Studies on preparation of ferro-zirconium (50%Zr) by open aluminothermic reduction of zircon were carried out on 200 gm (of zircon) scale. With the optimum charge composition, namely 200 gm zircon, 210 gm Fe_2O_3, 140 gm Al (15% excess over theoretical requirement), 50 gm $KClO_3$ and 140 gm of freshly burnt lime, well consolidated massive ferro-zirconium buttons were obtained. Zirconium recovery in the process was estimated at 90%.

2.3.4 Ceramic Grade Zirconia

(T.S. Krishnan, J.M. Juneja and P.R. Menon)

Commercial grade zirconium is used in the fabrication of ceramic materials. Two processes, one involving lime sintering and another soda ash sintering of zirconia were established. The processes involved treating zircon at high temperatures (1000-1400°C) with CaO, Na_2CO_3 so as to obtain dil. acid or alkali soluble silicates, which were leached out the product residue was zirconia with about 1% SiO_2. The product yields were 88-99%. It is planned to scale up the operation to 25 kg batches of zircon.

2.3.5 Graphite Coatings of Zircaloy Tubes

(T.K. Mukherjee, Sudhir Nanda and C. Narayanan)

The programme on coating of zircaloy tubes with graphite was continued using an alcohol based colloidal graphite suspension for the coating, followed by drying and baking treatment to obtain 10-15 thick adherent coatings. A number of tubes were prepared and supplied to different groups in BARC for the evaluation of acceptability. Various tests, both destructive and non-destructive, - including thermal cycling, autoclaving and stress corrosion cracking in iodine atmosphere - to test the quality of the coatings were carried out. The coatings have been found to be adherent, stable and protective. Further work is now being organised for tests under reactor environments.

2.4 HAFNIUM

(C.K. Gupta and I.G. Sharma)

For the preparation of hafnium metal, alternative routes to Kroll process were investigated. Experimental studies on calcium reduction and aluminothermic reduction of hafnium oxide, followed by refining processes like electron beam melting and electro-refining were carried out.

2.4.1 Refining of Calcium Reduced Metal

Calcium reduced hafnium powder was compacted at 250 kg/cm^2 pressure to pellets. The green pellets with 4.2 g/cc density were kept

in thoria containers and heated to 900 to 1800°C under a dynamic vacuum of 5 x 10^{-5} torr for a period of one hour, and the influence of sintering treatment on pellet density and purification of the metal was studied. A maximum sintered density of over 80% of theoretical was achieved at 1100°C, and effective removal of metallic impurities like iron, calcium, magnesium was observed. There was however no marked change in the interstitial impurity content in the pellets even after treatment at 1800°C.

The pellets sintered at 1100°C were melted in the electron beam furnace at 2 to 3 KW power level. The melting periods were varied to study the effect on the impurity content of the product. At 2.5 KW power level and 120 minutes melt-duration, metal buttons with hardness of 172 VPN were obtained, and there was a considerable decrease in metallic and non-metallic impurity levels, except for nitrogen.

The pellets sintered at 1100°C were also used in electro-refining studies. Using a NaCl-NaF, $HfCl_4$ melt, optimum conditions were established to achieve maximum current efficiency and product yield. A melt containing 4.5% soluble hafnium, operated at 860°C was found suitable. With an initial cathode current density of 72 amp/ft^2 maximum cathode current efficiency of 75% and average product yield of 60% were achieved. The product was found to be low in interstitials (126 ppm O_2, 10 ppm N_2 ; arc melted button hardness 150 VPN).

2.5 THORIUM

(C.V. Sundaram, J.C. Sehra and P.L. Vijay)

The studies on the preparation of ductile thorium metal by magnesium reduction of $ThCl_4$ followed by pyrovacuum treatment were completed. The operating parameters for the production of $ThCl_4$ from thorium oxalate, purification of $ThCl_4$, reduction of $ThCl_4$ and vacuum distillation of Mg and $MgCl_2$ were established, and the metal analysed: 847 ppm O, 20 ppm N, 179 ppm C, 100 ppm Mg, 49 ppm Fe, < 50 ppm Ni, 11 ppm Al, 7 ppm Cr (arc melted button hardness : 90 VPN).

2.6 TITANIUM

2.6.1 Treatment of ilmenite with $TiCl_4$

(Ch. Sridhar Rao and K. Swaminathan)

Experimental investigations on treatment of ilmenite ('Q' grade) with $TiCl_4$ aimed at the preparation of a beneficiated product and to understand the kinetics of the process in the fluidised bed reactor systems were continued. Experiments were carried out on 10 g scale in a silica tube reactor. The influence of reaction temperature, gas flow rate, $TiCl_4$ concentration and duration of treatment on the removal of iron oxides was studied.

In the temperature range (775-1000°C), it was observed that there was a marked change in the reaction rate at 900°C. The reaction was moderate in the temperature range 775-900°C and the activation energy was estimated at 21 K.cal/mole. At higher temperature (875-1000°C) the reaction was found to proceed at a faster rate and the activation energy was estimated at 68 K.cal/mole. The difference in the reaction rates was attributed to the presence of $FeCl_2$ which has higher vapour pressure at and above 900°C. In the high temperature region the conversion of iron ($1 - (1-x)^{1/3}$) Vs time (t) relationship was found to be linear till 95% conversion.

In the experiment on the effect of flow rate of total gas (argon and $TiCl_4$ vapours), it was found that maximum conversion occurred at 3000 cc/min. From the studies on the effect of initial concentration of $TiCl_4$ it was observed that the reaction follows first order chemical reaction. Further studies are being continued on the treatment of oxidised ilmenite with $TiCl_4$.

2.6.2 Magnesiothermic Reduction of Rutile in Hydrogen Atmosphere

(J.C. Sehra, I.G. Sharma and A. Unnikrishnan)

A programme aimed at the production of pure titanium from direct reduction of rutile followed by electro-refining of the metal was initiated. Experiments were carried out to reduce rutile with

magnesium in a closed vessel filled with hydrogen under a positive pressure of 20-30 cm of Hg.

500 gm of rutile mixed with magnesium (5, 10, 20% excess over theoretical) and $MgCl_2$ (20, 30, 40 wt% rutile) was kept in a retort and filled with hydrogen gas. The retort was heated to 1000°C and held at this temperature for 2-4 hours. At the end of the predetermined period the product was removed and leached with dil. acid solution. In a typical run lasting over 4 hours with excess Mg and appropriate amount of $MgCl_2$, metal powder with 90% yield was obtained.

The product metal powder was compacted at 250 kg/cm^2 pressure in the form of pellets and sintered at 1100°C under vacuum (0.03 micron pressure). The sintered pellets were used as anode feed in the electro-refining process. The electro-refining was carried out at 850°C in NaCl-$TiCl_2$ melt with 3% soluble Ti at different current densities. It was observed that a maximum current efficiency of 40% was achieved at a cathode current density of 360 amp/ft^2.

2.6.3 Fused Salt Electrolysis of $TiCl_4$

(Ch. Sridhar Rao, T.K. Mukherjee, C. Subramanian and K. Swaminathan)

Investigations on the preparation of titanium metal from $TiCl_4$ by its electrolysis in a fused NaCl-KCl melt were continued. A few experiments were carried out at 780-800°C for a duration of 11 hrs. at the Faraday/mole ratio of 6.5 and cathode current density of 400 amp/ft^2. The metal yield was low (40%) and the arc-melted button hardness 320 VPN. The failure to achieve good product quality and yield was attributed to disintegration of graphite anodes and their frequent failure in the operations.

2.6.4 Ferro-titanium

(D.K. Bose and O.K. Mehra)

Ferro-titanium with 20 to 40% Ti finds application in steel industry in the preparation of alloys. Experiments were carried out

to prepare ferro-titanium containing 35% Ti from ilmenite by open aluminothermic reduction process. The effect of Al content 0-20% excess over theoretical requirement, the live flux content (50-80% wt of ilmenite) on ferro-titanium yield and quality was studied. In a typical run with 200 gm ilmenite with 180 g Fe_2O_3, 150 gm Al and 120 gm CaO, a well separated button of ferro-titanium was obtained, at 90% recovery of titanium value.

2.6.5 Oxidation of $FeCl_2$ Aqueous Solution for Processing Ilmenite

(Ch. Sridhar Rao, C. Subramanian and K. Swaminathan)

$FeCl_3$ solution which is obtained by oxidation of $FeCl_2$ is used in beneficiation of minerals. A potential application of ferric chloride is in the aqueous processing of ilmenite for its beneficiation.

For the experimental studies, a thick walled glass tube 50 mm dia, 1500 mm long was used as the main reactor. An electric resistance heating tape was used to heat the tube. The tube was kept at an angle (5°) to the horizontal to permit flow of the liquid. The tube, the storage tank and the receiver tanks were pressurised with oxygen gas to a desired pressure.

250 ml of $FeCl_2$ solution containing about 25 gm dissolved iron was passed through the tube for each run. The effects of liquid flow rate (3.125, 5, 7.8 cc/min), pressure (40, 60, 80 psig) and number of passes (or duration) at the reactor wall temperature of 140-150°C were studied. The effect of initial pH (0.5, 1.5 and 2.5) of the solution and its variation after each treatment was also followed. The conversion was estimated by chemical analysis both for ferro content and total iron content after each processing stage.

The results indicated that pressure and flow rate but not pH had marked effect on conversion of $FeCl_2$. Further studies are being carried out to attain better conversions, especially with the half of catalyst like $CaCl_2$, NH_4Cl.

2.7 VANADIUM

Investigations on the development of processes for the recovery of vanadium values from industrial byproducts like (i) Bayers sludge, and (ii) vanadiferous slag were continued.

2.7.1 Treatment of Bayers Sludge

(C.K. Gupta, D.K. Bose and O.K. Mehra)

The Bayers sludge used in these investigations was received from M/s Hindustan Aluminium Company, Renukoot, U.P. Two alternative hydrometallurgical processes were established to recover vanadium values either as pure V_2O_5 or a complex calcium salt of vanadium. Yet another method was studied. In this process the sludge was dissolved in hot water (70-80°C) with the addition of H_2SO_4 to maintain the pH of the solution at 7/8. The neutral vanadium rich solution was treated with NH_4Cl at room temperature to precipitate ammonium metavanadate, which on calcination at 450°C resulted in pure V_2O_5. The product was analysed to contain about 98% V_2O_5.

2.7.2 Treatment of Vanadiferous Slag

(C.K. Gupta, D.K. Bose and O.K. Mehra)

Vanadiferous slag - a byproduct in the processing of titaniferous magnetites at M/s VISL, Bhadravati was used in these studies. The slag was treated both by pyro and hydrometallurgical methods to recover vanadium values.

The process involved salt roasting of the slag followed by its leaching to dissolve the vanadium content. Salt roasting experiments were carried out in a rotary kiln. The effect of roasting temperature (600-900°C), amount of salt-soda ash (10.20% by wt. of slag), duration of roasting (0.5 to 3 hrs.), presence of an oxidising agent ($KClO_3$) and the particle size (-60 +325 mesh) on vanadium recovery was studied.

It was observed that slag size of -100 mesh, 20% soda ash, 5% $KClO_3$ in the charge and roasting at temperature of 800°C for a period of 2 hours were optimum conditions for 98% vanadium recoveries.

2.7.3 Production of Vanadium Oxycarbide and its Evaluation as Steel Additive

(C.K. Gupta and D.K. Bose)

The suitability of vanadium oxycarbide as an alternative to vanadium carbide and ferro-vanadium as a steel additive was investigated.

Vanadium oxycarbide was prepared by controlled reduction of V_2O_3 with petroleum coke. V_2O_3 and petroleum coke powders were mixed and compacted to pellets. The pellets were heated to 1300°C in an electric resistance furnace, and held at ultimate vacuum of 500 torr.

The product obtained was found to be corresponding to empirical formula, $VO_{0.67-0.44}\ C_{.2-0.7}$. Such a product was used as a steel additive. The quality of the steel obtained were compared with those obtained by the addition of vanadium carbide or ferro-vanadium. Vanadium recoveries and solution times for all the vanadium additives were found almost similar. With vanadium carbide there was some pick up of carbon in the steel, as contrasted with vanadium oxycarbide from which carbon pick up was practically negligible.

2.8 NICKEL

(C.K. Gupta, T.K. Mukherjee and P.P. Shukla)

Investigations on recovery of nickel and copper values from a sulphide concentrate (6%Ni, 9%Cu, 20%Fe) supplied by the Uranium Corporation of India Ltd. were continued. Salt roasting and wet chlorine treatment processes were studied.

2.8.1 Salt Roasting Process

The salt roasting process which was established on 50 gm scale of the concentrate in static bed glass reactor was reexamined in rotary kilns in ½ kg batches. The major problem encountered in operating such a furnace was caking and sticking of the charge to the furnace wall leading to incomplete roasting. This problem was however solved by incorporating in the charge steel balls or rods which helped in

milling the agglomerated charge in the free-flowing powdery form.

Efforts were also made to conduct the roasting in a specially dessigned roaster. The roaster essentially consisted of a horizontally placed stationary mild steel reactor provided with a centrally placed baffled shaft to serve as a raker. This modified design was found satisfactory in conducting roasting operations.

A fresh batch of higher grade concentrate analysing 7.08%Ni, 17.8%Cu and 30%Fe was also processed by the salt roasting technique by varying the salt to concentrate ratio from 1 to 0.12. It was found possible to recover 93% of the nickel and 97% of the copper with nickel to iron ratio of 3.82 by using a salt to concentrate ratio of 0.5.

2.8.2 Chlorine Leaching

Detailed investigations were carried out to establish aqueous chlorination as a possible route for the processing of the sulphide concentrate. The process in brief consisted of passing elemental chlorine at ambient pressure in an agitated aqueous slurry of the concentrate.

The effects of pulp density (5 to 33 wt%), leaching temperature (25 to 100°C), amount of chlorine (1.25 to 4.56 gm per gm of the concentrate) and its rate of passing (40 to 160 cc/min) on nickel recovery were studied. It was found possible to recover 98% of the nickel and 72% of the copper value present in the concentrate by using a pulp density of 28%, a temperature of 60°C and 3 gm of chlorine per gm of the concentrate, passed at a rate of 80 cc/min. The leach solution was however found heavily contaminated with iron as about 70% of the iron got solubilized to a remedial measure, the concentrate was pre-roasted at different temperature (450 to 700°C) in a rotary furnace before chlorine leaching.

In comparison to the direct leach, roasting at 450°C followed by Cl_2 leaching required 75% less chlorine, the recoveries of nickel and copper were almost quantitative and the nickel-copper bearing solution was very low in iron.

In a variation of the process, efforts were also made to avoid roasting step by adopting a two stage Cl_2-O_2 leaching procedure. In this new technique chlorine leaching of the sulphide was accomplished at 40 psi pressure and temperature of 90 to 150°C in a glass-lined steel reactor to solubilize nickel, copper and iron followed by oxymixtures at same temperature and pressure to precipitate iron as hydrated iron oxide. The solution is under evaluation.

2.9 RARE EARTH - COBALT PERMANENT MAGNETS

Rare earth - cobalt permanent magnets of the $R(CO)_5$ type made of binary alloys of cobalt with cerium, samarium, preseodymium etc. are known to possess maximum energy products $(BH)_{max}$. These magnets are used as aircraft and aerospace instrument components. Optimisation of different routes for the production of Ce-Co and misch metal-Co alloy powders was carried out.

2.9.1 Direct Alloying Method

(T.S. Krishnan and R.P. Tangri)

The constituent components that is cerium and cobalt were arc-melted or induction melted in an alumina crucible and cast to ingots. The alloy obtained by these two melting methods were found to contain undesirable phases (R_2Co_5 / R_2Co_{17}) instead of wholly $R(Co)_5$ phase. The castings were crushed to powder and separated into separate size fractions. The powders of specific size fraction were compacted in a magnetic field and the magnetic properties were studied. Effect of particle size on the magnetic properties of the product was studied.

The Ce-Co alloy obtained by induction melting and casting was crushed to 10-15 micron size powder. The powder was pressed in 6 kOe field. The product material was found to give magnetic induction (Br) and coercivity H_c value of $>$1000 G and $>$1000 O_c respectively. Further studies on high field pressing followed by annealing and remagnetisation of the compacts are being explored.

Reduction-diffusion Process
(T.S. Krishnan, P.R. Menon and R.P. Tangri)

Development of the reduction diffusion process, a relatively economic route for the preparation of rare earth - cobalt magnetic material was investigated.

A charge consisting of cobalt and rare earth oxides were co-reduced with calcium metal in hydrogen gas atmosphere, to prepare $R(Co)_5$ type alloys. Influence of parameters like charge composition, particle size of constituents materials, reduction temperature, duration (reduction / diffusion) etc., on the product yield and the nature (composition/phase) of the product was studied. A charge consisting of rare earth oxide and 25% excess calcium was compacted at 30 tsi and heated to 1200°C. The reduction was carried out at this temperature for two hours. The reduced mass was leached and evaluated. Alloy powder with 95% yield rich in $R(Co)_5$ phase was obtained.

2.10 METAL POWDERS

Sub-micron and micron size metal powders are useful in making high density sintered compacts. Investigations were carried out to prepare fine size Mo and W powders by hydrogen reduction of their oxides and oxychlorides.

2.10.1 Molybdenum
(C.K. Gupta, T.K. Mukherjee and P.V.S. Pillai)

Pure molybdenum oxychloride was prepared by low temperature (300°C) oxychlorination of molybdenum concentrate. The oxychloride was distilled in a pyrex reboiler and was allowed to pass through a silica tube reactor. Hydrogen gas was also admitted into this tube. Number cyclone type of condensers and collectors were used to receive the metal powder. It was also possible to develop the metal coating on surfaces by this method.

In a typical run, molybdenum oxychloride was distilled at the rate of 30 gm/hr and passed through the reactor tube held at 900°C and

reduction carried out by passing 300 cc/min of hydrogen. Submicron size molybdenum metal powder was obtained.

400 gm of high purity molybdenum powder was also prepared by hydrogen reduction of molybdic oxide at 1000°C in an externally heated reactor tube.

2.10.2 Tungsten

(T.K. Mukherjee and P.P. Shukla)

Chemical precipitation was investigated to prepare submicron size tungsten powder. In the chemical precipitation technique a saturated solution of ammonium tungstate was slowly added to M nitric acid which was kept stirring. The precipitate was filtered, dried and calcined to obtain tungstic acid which was reduced with hydrogen at 750°C. The powder (-400 mesh) is under evaluation.

2.11 THERMOCHEMICAL AND THERMODYNAMIC STUDIES

2.11.1 Refining Tantalum by Carbon Deoxidation and Sacrificial Deoxidation

(S.P. Garg, N. Krishnamoorthy and R. Venkataramani)

The relative extent of carbon deoxidation (as CO) and sacrificial deoxidation (as TaO) was investigated with a view to purify tantalum metal with respect to oxygen impurity.

Tantalum powder containing 5000-6000 ppm oxygen was mixed with required amount of carbon and pelletised. The pellets were heated to high temperatures in an induction furnace under vacuum. The effect of temperature (1650-2050°C), order of vacuum (1.5×10^{-4} 5×10^{-5} torr pressure), oxygen to carbon ratio (1.0 - 1.5) and duration (1-4 hours) on the extent of deoxidation was studied. The samples were analysed at various stages for their oxygen and carbon contents.

It was observed that temperature and pressure have great effect and substantial deoxidation occurred only above 1800°C at $1.5 \times 10^{-4} - 5 \times 10^{-5}$ torr pressure. It was also observed that oxygen was first recovered as CO till the carbon content was 300 ppm and then sacrificial deoxidation occurred. In a typical run carried out at 2050°C

with O/C ratio 1.05, 5×10^{-5} torr pressure for 2 hours, a product containing 100 ppm carbon and 200 ppm oxygen was obtained with negligible loss of metal values.

2.11.2 High Temperature Reaction between Nb_2O_5, NbC and TiC
(S.P. Garg, N. Krishnamoorthy and R. Venkataramani)

The study of reaction between Nb_2O_5, NbC and TiC as per the equation

$$\frac{1}{5} Nb_2O_5 + (5 - x) / 5 \ NbC + \frac{1}{5} TiC = \frac{1}{5} Nb_{7-x} Ti_x + CO$$

was continued. It was aimed to investigate the titanium deoxidation tendency in Nb and also to prepare Nb-Ti alloys.

Pellets of the components containing oxygen/carbon ratio 1.01 : 1.1 and titanium content of 5 to 30 atm % were heated upto 1900°C in an induction furnace under vacuum (10^{-4} torr) and then melted in electron beam furnace to obtain buttons.

It was observed that near complete removal of titanium and oxygen occurred during the reaction stage irrespective of initial charge composition. Oxygen was removed mainly as $TiO_{(g)}$ x O (g) with no loss of niobium. When Ti content was more than 15 atom %, TiO evaporation rate was found higher than CO thus resulting in a product richer in carbon. In a typical run with O/C ratio 1.05 and 5 atom % Ti, a product (Nb) containing $<$ 1000 ppm C, 300 ppm O, and 800 ppm residual Ti was obtained. It was concluded that Nb-Ti alloy could not be prepared, though purification of Nb with respect to oxygen due to evaporation of TiO could be achieved.

2.11.3 Preparation of Uranium Silicides and Thermodynamic Properties of USi_3
(S.P. Garg and Y.J. Bhatt)

Uranium forms a number of important refractory compounds USi_3 USi_2 , U_3Si_5 , USi , U_3Si_2 and U_3Si with silicon which are of interest to the atomic energy programme. Preparation of these compounds by

silicothermic reduction of UF_4 and thermodynamic studies of USi_3 have therefore been investigated.

A mixture of UF_4 and silicon powder was charged in a tantalum crucible and heated at a constant heating rate of 6°C/min under vacuum in a vacuum thermoanalyser. The thermogravimetric and the differential thermogravimetric analyses indicated that the reaction proceeds in the following sequence :

$$4\ UF_4 + Si \rightleftharpoons 4\ UF_3 + SiF_4 \quad \ldots\ldots \quad (i)$$

$$4\ UF_3 + 15\ Si \rightleftharpoons 4\ USi_3 + 3\ SiF_4 \quad \ldots\ldots \quad (ii)$$

$$4\ UF_3 + 11\ USi_3 \rightleftharpoons 15\ USi_2 + 3\ SiF_4 \quad \ldots \quad (iii)$$

$$4\ UF_3 + 29\ USi_2 \rightleftharpoons 11\ U_3Si_5 + 3\ SiF_4 \quad \ldots \quad (iv)$$

The last step upto the U_3Si_5 stage (reaction iv) goes to completion on holding the charge at 950°C under vacuum (10^{-2} to 10^{-3} torr). The preparation of lower silicides (USi, U_3Si_2 and U_3Si) by this process would require heating the charge further above 1000°C and has not been attempted as UF_3 itself has an appreciable pressure above this temperature. Thus only the silicides USi_3 to U_3Si_5 can be prepared by this process.

The standard free energy change of the reaction (ii) has been determined by the measurement of equilibrium pressure of $SiF_4(g)$ over the mixture of UF_3 + Si + USi_3 employing static method of vapour pressure measurements. From these measured values and from the reported free energy of formation of $UF_3(s)$ and $SiF_4(g)$ the standard free energy of formation of $USi_3(s)$ has been calculated between 870 to 1040°K and can be represented as

$$\Delta G^{\circ}_{USi_3} = -32470 + 0.50\ T \text{ cals / mole}$$

These investigations were carried out in collaboration with Shri D.D. Sood and Shri Rajendra Prasad of Radio Chemistry Division.

2.11 Thermodynamic Studies of WC by Isopiestic Technique

A programme was initiated to investigate the thermodynamic properties of WC by an isopiestic technique. The method involved the equilibration of a mixture of WC and tungsten with pure iron pieces sealed in a quartz capsule containing trace amount of hydrogen. The equilibrium was achieved through the following reversible reaction:

$$\underline{C}\ (\text{in WC or Fe}) + H_2 \rightleftharpoons CH_4$$

Since the activity of carbon in the WC + W mixture and in iron will be same, the activity of carbon in the (WC + W) mixture was determined from the carbon content of iron at equilibrium. The free energy of formation of WC (ΔG°_{WC}) was determined making use of the concentration-activity relationship for dilute Fe-C alloy available from the literature. From experiments carried out at 1196 and 1302 K, the ΔG°_{WC} values were estimated as -7270 and 6860 cal/mole respectively. Further work is under progress.

2.12 STUDIES ON FLUIDISED BED SYSTEMS

(Ch. Sridhar Rao and D. Sathiyamoorthy)

Fluidised bed systems, particularly of the solid-gas type, can be used for physical operations and for carrying out chemical reactions of metallurgical interest. Studies were undertaken on the design of gas distributors in gas-solid fluidised beds. A theoretical model to design the multiorifice plate gas distributors was proposed. Experimental investigations were carried out to establish the design equation.

Experiments were carried out in a 100 mm dia(D) glass tube assembly, consisting of 20 (N), 3 mm dia orifice holes. Gas flow (compressed air) through each orifice was noted by means of orifice meters incorporated in each distributor orifice line. Total air flow

(U) and pressure drops across the bed (BP 6) and the distributor (BPd) were noted. Zircon, rutile and alumina powders were used as bed material. The number of operating orifices (n) with respect to air flow rate (O-Umf-UM) and bed height (1 to 7D) were recorded.

Equations of the following type were derived :

$$K = \frac{n}{N} \frac{Umf}{U-Umf} \quad , \quad K = KO \sqrt{\frac{\Delta Pd}{\Delta Pb}}$$

where K and KO are system dependent and system-independent constants. Methods for predicting KO and $\frac{\Delta Pd}{\Delta Pb}$ were also proposed. From the experimental results, validity of the above equations was proved and values of KO were determined for each set of experimental conditions. Least square values were determined for all the set of experiments under N = N condition which resulted in an equation of the form

$$K = 0.65 \left(\frac{\Delta Pd}{\Delta Pb}\right)^{.43}.$$

Thus having known the $\Delta Pd/\Delta Pb$ rate for a system U_M and finally the ΔPd and the orifice plate could be designed. Based on these studies a gas distributor for a high temperature process is being designed.

2.13 DEVELOPMENT OF PLASMA FURNACE

(T.K. Mukherjee and S. Nanda)

A programme was initiated to develop a plasma furnace which could generate temperatures of 2000°C. Such furnaces are useful in the beneficiation of ores and extraction of metals.

A laboratory scale induction-coupled-plasma furnace using argon gas was designed and fabricated. The furnace consisted of a 37 mm dia x 600 mm long transparent silica tube. An induction coil was wound round the tube. R.F. power supply was used to generate the heat. Argon gas supply ports and material feed ports were provided at the top end of the silica tube. A 200 mm long water cooled assembly, at the lower end of the tube formed the product collector. Blank test

runs were carried out and the temperatures of the order of 2000°C were achieved. Further work on treatment of ores and minerals is in progress.

2.14 BERYLLIUM PILOT PLANT PROJECT
(C.V. Sundaram, C.M. Paul, B.P. Sharma and K.S. Subbarao)

2.14.1 Project Report

The Departments of Electronics and Space have emphasised the need for the setting up of an indigenous facility for the production of copper-beryllium alloys and beryllium metal at an early date. Extensive demand surveys carried out by various groups have placed the present annual requirements at about 10 tonnes of copper-2%beryllium alloy and 250 kg of beryllium metal. Accordingly a project report was prepared, in June, 1977, for the setting up of a Pilot Plant to produce 10 tonnes of copper-2%beryllium alloy ingots and 250 kg of vacuum hot pressed(VHP) beryllium per year blocks in single shift operation. (The Plant could be operated in 3 shifts when the demand increases. The June, 1977 Project Report was prepared on the premise that the Pilot Plant will be set up at the new BARC site at Vashi (New Bombay), an an independent facility having its own electric substation and other ancillary facilities.

The June '77 Project Report has formed the basis for a Memorandum of Understanding between the Departments of Atomic Energy, Electronics and Space. It has been decided that the Pilot Plant will be engineered, erected, commissioned and operated by BARC personnel and the necessary capital and operating funds will be provided by the Departments of Electronics and Space. The financial sanctions for the project have been received from DOS and DOE.

2.14.2 Civil, Electrical and Ventilation Works

Based on the preliminary equipment layout drawings and electrical and ventilation requirements finalised by the Beryllium Project group, tender drawings for civil, electrical and ventilation works for the Beryllium Pilot Plant were prepared by the Civil Engineering and Technical Services Divisions.

2.14.3 Procurement of Equipment and Materials and Recruitment of Staff

Indents for materials required in advance for fabrication of equipment and for long delivery items were raised. Purchase orders for the supply of stainless steel materials were released. Specifications for other equipment were detailed. Action was also initiated for the recruitment of staff urgently required for the project.

2.14.4 Conversion of Copper-Beryllium Alloy Ingots

Whereas the Beryllium Pilot Plant will produce cast beryllium-copper alloys in the form of 15 kg ingots, for end applications in the electrical and electronic industries these alloys would be finally required mostly in the form of thin foils and sheets and to some extent as wires and rods. It has been suggested that since the quantities of coppe r-beryllium alloys produced annually are relatively small, it would be better to entrust the conversion of ingots to the final shapes, to other organisations which have the necessary capability and capacity.

In the above context a meeting was held with the members of the Advisory Council, from the Department of Electronics, the Beryllium Project group and M/s Bralco Metal Industries, Bombay, (one of the leading producers of sheets and foils of copper and copper base alloys in India) in September 1977 to discuss on the conversion of copper-beryllium alloy ingots to finished shapes and to formulate basis for further negotiations on the terms and conditions of contract. It was decided at the meeting to roll some test ingots, at M/s Bralco's rolling facility, in order to standardise the various rolling parameters. Work was accordingly initiated to study the hot and cold rolling of copper-beryllium. Twenty kilogram ingots of Cu-2%Be alloy, (210 mm x 160 mm x 65 mm thick) were successfully cold rolled at 750°C to 6 and 10 mm thick strips. The strips have been annealed and scalped preparatory to further cold rolling.

2.14.5 Copper-Beryllium Alloys - Demand Survey

In order to obtain a fresh compilation of information, regarding the quantity requirements and detailed technical specifications of copper-beryllium alloys required by the actual users, a comprehensive standard format was prepared and circulated to the users through IPAG (Electronics Commission). The compilation of the results of this market survey will provide a basis for rationalising the various specifications of copper-beryllium alloys into a small number of standard specifications that will be acceptable to the majority of the users. The compilation will also provide the basis for holding discussions with organisations which are likely to be entrusted with the conversion of the alloy ingots, produced in the Pilot Plant, to various finished forms.

2.15 PROCESS DEVELOPMENT

2.15.1 Preparation of Anhydrous Beryllium Fluoride from Indian Beryl

(C.M. Paul, K.S. Subbarao and S.A. Kulkarni)

About 1000 kg of beryl lumps have been ground to -200 mesh by ball milling, operated in close circuit with rake classifier.

Studies have been continued on the silico-fluoride sintering of beryl for conversion of beryllium values of beryl into water soluble form on a 500 g BeO scale. It has been found that by sintering at 750°C for 2 hours followed by water leaching of the wet ground sinter, with a water to solid ratio of about 3 : 1, about 97% of the beryllium values of beryl could be recovered in the water soluble sodium beryllium fluoride.

Preparation of beryllium hydroxide by sodium hydroxide treatment of sodium beryllium fluoride leach liquor followed by filtration in a stainless steel plate and frame filter press has been studied on a 150 g BeO scale and the overall beryllium recovery has been observed to be around 97.5%. In another experiment beryllium oxide having a purity as high as 99% has been successfully prepared on a 150 g scale

by precipitating sodium beryllium fluoride leatch liquor (5.5 g BeO per litre) with 20% NaOH solution. The hydroxide was first dried at 200°C and then calcined at 900°C.

Studies have also been carried out on the recovery of fluorine values from the filtrate containing NaF, obtained in the filtration of $Be(OH)_2$. It has been found that pH has a profound influence on the recovery. The fluorine recoveries have been found to be 91% and 96% in the case of $Fe_2(SO_4)_3$ and $FeCl_3$ respectively at a pH of 5.

Based on the earlier operational experience on the decomposition of ammonium beryllium fluoride, a modified decomposition assembly consisting of a nichrome wound resistance furnace, inclined graphite decomposition tube, stainless steel screw feeder and water cooled nickel condenser was designed, fabricated and commissioned. The assembly has the capacity to produce 500 g BeF_2/hour. The decomposition zone of the inclined graphite tube is maintained at a temperature of 900°C. Ammonium beryllium fluoride is introduced progressively with the help of a screw feeder through a tube passing through the nickel condenser. Molten beryllium fluoride which flows out through a hole at the bottom of the inclined graphite tube is collected in a graphite mould. With this system it has been possible to prepare BeF_2 with a recovery of about 95%.

2.15.2 Preparation of Beryllium and Copper-Beryllium Alloys
(C.M. Paul, B.P. Sharma, V.D. Shah and M.G. Rajadhyaksha)

A silica tube vacuum induction melting unit was designed and fabricated for vacuum melting beryllium pebbles. The silica tube is flanged at both ends and sealed with neoprene gaskets. The system is evacuated through the bottom flange with a combination of oil diffusion pump and a rotary pump, while the top flange supports a view port. Beryllium is melted in a beryllia crucible by indirect induction heating using a graphite crucible as a susceptor, and is allowed to solidify in the crucible itself. With this assembly beryllium pebbles

have been melted and purified on a scale of 250 gm, under a dynamic vacuum of 10^{-3} torr at a recovery of 92%.

Preliminary designs of a vacuum induction melting and tilt pouring furnace, with a effective crucible volume of about 1.7 litres, for the purification of beryllium pebbles and a vacuum hot pressing unit for fabrication of 100 mm dia x 100 mm long beryllium blocks have been completed.

About 40 kg of copper-beryllium master alloys containing about 8.5% Be have been prepared in 5 and 6 kg batches at a beryllium recovery of about 85%. The reduction of BeF_2 (25% excess over theoretical) was carried out at about 1000°C for 2 hours with magnesium in the presence of copper. The final temperature of the charge was brought to 1400°C to effect better slag metal separation. The master alloy was cast in graphite moulds. The BeF_2 present in the slag was recovered by water leaching.

Cu-2%Be and Cu-0.7%Be alloys were prepared by diluting the master alloy with appropriate amount of copper in a induction melting furnace. Casting recovery and soundness of cast could be considerably improved by reducing the shrinkage pipe by improving the mould tundish design. While casting a slab of 160 mm x 65 mm cross section, the shrinkage pipe could be almost completely eliminated by maintaining a tundish hole diameter of 8 mm and by preheating the tundish to 450°C with the help of blow torches.

In response to a request from VSSC, Trivandrum about 100 kg of Cu-0.5%Be - 2.7%CO alloy ingots have been supplied.

About 25 cast billets of Cu-2%Be and Cu-0.7%Be, each weighing about 3 kg, have been hot extruded at 750°C, at Atomic Fuels Division, to 27 and 37 mm diameter rods, after proper solution treatment and machining. Limited quantities of these rods were supplied to M/s Escrots, New Delhi, M/s PeeVee Precision Works, Madras, and to Combat Vehicles Research and Development Establishment, Avadi in response to their urgent requirements.

3. PHYSICAL METALLURGY

Physical Metallurgy Section continues to pursue basic studies in physical, mechanical and structural properties of metals and alloys of interest to the nuclear energy technology. One important aspect that is emphasised is the understanding of the structure-property correlation in many of the systems.

Basic investigations on the deformation behaviour of zirconium and zirconium-oxygen with respect to grain size and temperature of deformation have been conducted. A potential pressure vessel steel is being evaluated for various mechanical properties so as to ascertain its usefulness in as-reactor material applied problems such as diffusion bonding, and pressure bonding techniques are being studied to evolve suitable methods for making composite plates.

Phase transformation studies and influence of structure on the mechanical properties, utilising transmission and scanning electron microscopy and instron testing machines have been made. A large volume of interesting data on a number of binary and ternary systems of zirconium based and titanium based alloys, have been collected

A general theory of transformation structure is emerging from these studies which would enable one to predict may useful alloy systems for special applications.

Diffusion studies, involving intrinsic and interdiffusion phenomenon have been continued and valuable datahave been collected. Analysis of these data have led to the generalization of the theory of diffusion in metals in general and zirconium in particular. Irradiation and its influence on mechanical properties on metals and alloys has been continued with a view to understand the defect generation, annihilation as reflected in the gross property changes.

Physical Metallurgy Section has been rendering service to various organizations regarding failure analysis, metallographic evaluation of structural components, alloy making etc.. The Section has also undertaken many an applied problem of interest to the nuclear energy programme.

3.1 MECHANICAL METALLURGY

3.1.1 Deformation Behaviour of Zirconium Alloys

(i) The Influence of Deformation Twins on the Tensile Properties of Zirconium-2.5wt%Nb Alloys

(M.K.Asundi, T.K. Sinha and J.K. Chakravarthy)

It has been observed in zirconium and zircaloy-2, that the occurrence of a small volume fraction of twins by low temperature deformation, improved both the strength and the ductility of the material, deformed at room temperature. The objective of the present programme was to study the influence of the deformation twins on the tensile properties of zirconium-2.5% niobium alloys.

In order to study the twinning behaviour, it was necessary to develop a well-defined grain size in the specimens by suitable heat-treatments. A heat-treatment schedule of vacuum annealing at 850°C for 5 hrs, was selected. Microstructures of the annealed samples consisted of equiaxed α grains of about 44 μ size and transformed β grains having Widmannstatten type morphology. Tensile tests were carried out at 77 K-300 K at nominal strain rates of 10^{-3} to 10^{-1} min^{-1}. The occurrence of twins were evident from the sharp load drops in the load-elongation diagram and the audible twin cry associated with twin initiation. The initiation of twins was found to be accompanied with very rapid work-hardening rate. The presence of twins was further confirmed by the optical microscopy using anodising etching techniques. It was noted that the occurrence of twins was strongly dependent on temperature and strain rate but defomation twins did not embrittle the material as was evidenced from the ductility values and the SEM examinations of the fractured surfaces. TEM work is in progress to study the twinning characteristics which will enable more meaningful correlation of mechanical properties with types of twins present.

(ii) The Deformation Twinning Behaviour of Zirconium-Oxygen Alloys

(V.Raman, T.K. Sinha and M.K. Asundi)

The objective of this work was to study the influence of interstitial element (oxygen) and the grain size on the deformation twinning behaviour of zirconium. Zirconium-oxygen alloys containing 100-1600 ppm of oxygen and grain sizes varying from 5 μ to 75 μ were tested under compression at temperatures varying from 77 to 298 K and using a nominal strain rate of 10^{-4} $min.^{-1}$. Twinning was observed only at an intermediate range of grain sizes varying between 15-25 μ , and only in alloys containing 300 to 800 ppm of oxygen. The results are being analysed to correlate the deformation twinning behaviour with composition and grain size, by determining the twinning frequency and nature of twins, by metallographic techniques.

(iii) Studies on structure-property correlation in a zirconium-4.6 wt% aluminium alloy

(V.Raman, P. Mukhopadhyay and S. Banerjee)

Attempts were made to correlate the earlier reported strengthening of Zr-4.6wt%Al alloy with microstructures in the light of the existing theories of alloy hardening. In order to explain the strength of beta quenched alloy, theories of solid solution hardening were utilised to calculate the approximate yield stress. The high strength of the alloy treated at the lower temperature(650°C) could be explained in terms of the contribution from the coherency strains associated with the state of order within the metastable particles. The strengthening contributions due to the lamellar α -Zr and Zr_3Al were analysed on the basis of Ashby's theory of plastically inhomogeneous materials and the calculated strengths compared favourably with the observed strength. The strength of the alloy was found

to decrease appreciably with increasing thickness of the second phase lamellae. The work hardening behaviour was analysed on the basis of Ashby's work hardening theory.

It is proposed to study the temperature and strain rate dependence of this alloy in three heat treated conditions.

(iv) Grain Size Effects in Zirconium-Oxygen Alloys
(V. Raman and P. Dasgupta)

The Hall-Petch slope for Zr-O alloys with 100 to 1600 ppm oxygen and 5μ - 15μ grain size as a function of strain (K_ϵ) was found to show peaks in the curves. These maxima occurred at lower plastic strains in low oxygen alloys, while higher oxygen alloys manifested these at higher plastic strains. The plots of K_ϵ vs ϵ_p for the 800 ppm alloy at room temperature showed a continuous decrease while that of friction stress σ_0 against ϵ_p showed a monotonic increase. This trend was more pronounced at lower temperatures. The variations of σ_0 and K_ϵ with oxygen content exhibited both maxima and a minima at some levels of oxygen. The above findings were rationalised in the light of the models available for grain size effects and strengthening.

(v) Structure and Strength of Dilute Zirconium-Copper Martensites
(S.L. Wadekar, V. Raman and P. Mukhopadhyay)

The morphology, the substructure and the strength of dilute zirconium-copper martensites were examined. The martensite obtained on rapidly quenching the alloys from the beta phase fields was found to have a lath morphology and a dislocated substructure. Precipitation at the lath boundaries could not be suppressed by this quenching treatment. These precipitates did not have the stoichiometry of the equilibrium Zr_2Cu. The strength of these martensites was found to increase substantially with increasing

additions of copper. This strengthening was due both to solid solution hardening and to the distribution of precipitates at the lath boundaries. The work hardening of dilute zirconium-copper martensites could be analysed in terms of Ashby's theory of the deformation of plastically inhomogeneous materials. The temperature dependence of the flow stress at any given level of plastic strain indicated that the addition of copper enhanced mainly the athermal component of the flow stress.

3.1.2 Mechanical Properties of a Prospective Reactor Vessel Steel of ASTM Designation HY-130
(T.K. Sinha, J.K. Chakrabarthy and M.K. Asundi)

This research project was undertaken to study the influence of microstructure on the flow and fracture behaviour of a potential nuclear pressure vessel steel; a low carbon alloy stell of 5 Ni-Cr-Mo-V type.

The available literature shows that this steel possesses an excellent combination of properties such as high strength, high toughness, good weldability and hardenability through a thickness of 4". In addition, this steel in quenched and tempered conditions, has not only initial low NDT, but also very low radiation enhanced NDT shift.

Two ingots of the nominal composition 5% Ni, 0.5%Cr, 0.5% Mo, 0.5%Mn, 0.1% V and 0.13%C, and balance Fe, were prepared by vacuum induction melting. Microstructure of the cast ingots showed fairly homogeneous dendritic structure and the hardness of cast ingots were 260 ± 10 VPN. Although this steel showed high work-hardenability and a 20% cold reduction increased hardness from 260 to 310 VPN, it showed satisfactory hot workability and could be hot-rolled into strips of 1 mm thickness, from a hot-forged ingot of 30 x 25 x 150 mm size. Microstructure of hot worked strip appeared to be bainitic in nature.

The influence of heat-treatments on the structure has been studied. While annealed samples showed a hardness value of 270-290 VPN, both the quenched and the normalised (Air cooled from austenitising temperatures) samples resulted in the hardness values in the range of 400-430 VPN, indicating the air hardening characteristics of this steel in very thin sections. The microstructure in the quenched normalised conditions, appeared to be martensitic and/or bainitic in nature and that of annealed ones, appeared to be transformed carbide or intermetallic phases distributed mostly at the grain boundaries and within the prior austenite grains.

The tempering behaviour of this steel has been studied to evaluate both the effects of time and temperature on the hardness values and the microstructures. Martensitically transformed specimens were tempered in the temperature range of 300-700°C (at an interval of 100°C) and the tempering times of 1 hr and 2 hrs. at each temperature. Tempering response has been studied both by the plot of hardness variation with temperatures at various times as well as by the plot of hardness values against Hollman-Jaffee parameters. These results indicated that the material possesses good tempering resistance although there was no evidence of secondary hardening in the high temperature region. Transmission electron microscopic work is in progress to correlate microstructures with these observations. Exhaustive experimentation is also underway to correlate tensile, stress rupture and impact toughness properties with microstructures of this material.

3.1.3 Solid State Welding of Zircaloy-2 Plates

(V. Raman, R. Kishore, J.K. Chakravarthy and M.K. Asundi)

(i) Pressure Welding of Zircaloy-2

Modifications were carried out on an existing equipment used for pressure welding runs. These were necessary in order to control accurately the different parameters in bonding experiments.

Experiments were conducted varying the temperature the pressure applied, and the time of application of pressure in a systematic way. The zircaloy-2 plates, used in these experiments were 25 mm square coupons, 0.5 mm thick. The surface of the coupons was polished since it is known that the surface condition of the zircaloy has a significant influence on the bond quality.

Trial experiments indicated the following conditions to be suitable for effecting a good bonding between two test plates:

Temperature - 850°C ; Pressure 200 psi and
Time : 30 mins.

This condition was based on metallographic examination of the sectioned pieces, which showed that the grains were continuous across the original interface.

(ii) Eutectic Diffusion Bonding

Eutectic diffusion bonding has been reported to be an inexpensive method with the possibility of achieving high bond strength. This process involves the formation of a molten eutectic layer of zirconium and a bonding agent such as copper between the zircaloy surfaces to be joined and the subsequent diffusion of the eutectic forming elements until the zircaloy matrix is continuous across the bond interface.

Experiments were carried out to establish the feasibility of this technique as a method for fabricating plate type fuel elements. The effects of various fabrication parameters on the bonded samples were looked into. The fuel elements samples comprised three basic components - zircaloy receptacle plates, cover sheets and fuel-wafers containing uranium-dioxide. Fabrication procedures included plating of the receptacle plates with the bonding agent and coating of the fuel with a barrier material to prevent the reaction between the fuel and the clad. A procedure to dip-plate copper on zircaloy-2 was standardised. It was found

that an oxidising treatment preceding the dip facilitated the development of a thin (0.5μ) adherent uniform film on the receptacle plates. Some experiments were also conducted employing graphite powder as a barrier material between the fuel and the zircaloy plates to inhibit reaction between them. On the basis of these experiments, it was possible to establish the following optimum parameters for eutectic diffusion bonding of zircaloy-2.

Temperature	1000°C	
Pressure	25 psi	[The application of pressure is necessary only to ensure intimate contact between all components]
Time of application of pressure		: 15-20 minutes
Thickness of the bonding agent		: 0.5 microns

These experimental conditions permitted excellent bonding between the plates and the complete disappearance of copper at the interface, presumably by diffusion into the bulk. The experiments were conducted on 3" x 3" samples.

Efforts to quantify such results and determine the strength of the bond are underway. Radiographic examination of the elements is also being done to evaluate the integrity of fuel pellets after the bonding operation. Fuel-clad interactions are also being studied.

(iii) Gas Pressure Bonding

An equipment has been fabricated and one trial run taken for the gas pressure bonding of large size (12" x 6") fuel elements. Such a procedure has all the advantages of an isostatic method.

3.1.4 A New Method for the Evaluation of Internal Stress from Stress-Strain Transient
(V.V. Raman and M.K. Asundi)

The methods hitherto in use for the determination of internal stress in materials were handicapped from certain limitations, either from the scope of validity of assumptions or from the experimental shortcomings. In order to avoid the handicaps, a new method was developed which is free from the assumptions except those which are the most general and the most widely accepted. The only experimental requirement is a tensile testing machine with which the specimen can be loaded continuously at a constant extension rate.

The present method defines a variable $\tau = \epsilon_p/\dot{\epsilon}_p$ where ϵ_p is the plastic strain and $\dot{\epsilon}_p$ its differential with respect to time during the stress-strain transient. It can be shown that $\tau = 0$ when the applied stress equals to internal stress. From a plot of log $\dot{\epsilon}_p$ against log ϵ_p one can find the slope at various points. A function $F = 1/1-\frac{d\ln\dot{\epsilon}_p}{d\ln\epsilon_p}$ can be evaluated for various points for which the values will also be different. When $\tau = 0$, F will be equal to 2.0. The integral $\int_0^{\tau} F d\tau$ gives the time during which the specimen has been undergoing plastic deformation. From this the internal stress can be evaluated.

In Zr-2.5%Nb this method was used and the result was compared with the one obtained by incremental unloading. The value obtained by the present method is much lower than the one obtained from incremental unloading. This is in accordance with the observations in published literature, where after correction for machine relaxation the value is much lower than the one evaluated without correction.

3.2 STRUCTURAL METALLURGY

3.2.1 Phase Transformations in Zirconium Alloys

(i) Active Eutectoid Decomposition in Near-Eutectoid Zirconium-Copper Alloys

(P. Mukhopadhyay, E.S.K. Menon, S. Banerjee and R. Krishnan)

In continuation of the work mentioned in an earlier report, the decomposition of the beta phase and the consequent formation of the intermetallic Zr_2Cu phase ($MoSi_2$ structure) in a Zr-1.6wt%Cu alloy has been examined in detail. It has been observed that eutectoid decomposition occurs very rapidly and cannot be suppressed even by fast beta quenching. The quenched structure consists of a lamellar aggregate of the alpha phase and a partially ordered, body centred cubic, metastable phase. The correspondence between the parent beta and the product alpha lattices is the same as that observed in the martensitic beta to α' reaction in zirconium alloys. There exists an one to one correspondence between the beta and the metastable phases. It has b een possible to propose a mechanism for this active eutectoid decomposition on the basis of the crystallographic and the microstructural data obtained from this study. The reaction appears to be a hybrid of martensitic and diffusion controlled processes. The metastable phase has been found to attain the structure and the stoichiometry of the equilibrium Zr_2Cu phase on tempering the beta quenched alloy. The orientation relationship between the equilibrium eutectoid products is :

$$(0001)_\alpha \parallel (013)_{Zr_2Cu}$$

$$[\bar{1}100]_\alpha \parallel [0\bar{3}1]_{Zr_2Cu}$$

(ii) Precipitation of $ZrCr_2$ in a Zr-1.9 at%Cr Alloy
(P. Mukhopadhyay, V. Raman, S.J.Vijayakar and S.Banerjee)

The precipitation of the topologically close packed Laves phase $ZrCr_2$ ($MgCu_2$ structure) in a martensitic matrix has been examined in this alloy. The martensite formed on beta quenching has a plate morphology and a dislocated substructure. Neighbouring martensite crystals are often twin related, the twin plane being the $\{10\bar{1}1\}$ type. The precipitation of $ZrCr_2$ precipitates cannot be suppressed by rapid beta quenching. Tempering at low temperatures gives rise to a bimodal precipitate size distribution. A significant amount of precipitate coarsening occurs on ageing the beta quenched alloy at 700°C. During tempering at this temperature, the martensite undergoes recovery and recrystallisation, the shapes of the recrystallised grains being determined by the distribution of heterogeneously nucleated $ZrCr_2$ precipitates formed during beta quenching and during the early stages of ageing. The orientation relationship between the alpha and the $ZrCr_2$ phases has been established as :

$$\{0001\}_\alpha \; // \; \{011\}_{ZrCr_2}$$

$$\langle 1\bar{2}10\rangle_\alpha \; // \; \langle 1\bar{1}1\rangle_{ZrCr_2}$$

(iii) Martensitic and Precipitation Reactions in a Zr-5wt%Ta Alloy
(E.S.K. Menon, P. Mukhopadhyay and S. Banerjee)

The martensite produced on beta quenching this alloy has been found to have an internally twinned plate morphology, the twinning being on the $\{10\bar{1}1\}_\alpha$ planes. Arrays of dislocations lying along these planes have also been observed and it appears that in addition to the $\{10\bar{1}1\}$ twinning shear, a slip shear on a different variant of the $\{10\bar{1}1\}$ planes is operative as an

inhomogeneous shear system during the martensitic transformation. Depending on the ageing temperature, two different precipitation sequences have been encountered while tempering the beta quenched alloy. At temperatures lower than the monotectoid but not far below it, the metastable, zirconium-rich β_I phase precipitates in the α' matrix. At still lower temperatures, the equilibrium, tantalum-rich β_{II} precipitates emerge. Preferred sites for precipitate nucleation are the interfaces associated with the martensite structure : plate and twin boundaries. These observed precipitation sequences have been rationalised in terms of the free energy versus composition plots generated from the analysis of the zirconium-tantalum phase diagram. The orientation relation between the α and the β_I phases has been found to be :

$$(0001)_{\alpha} \quad // \quad (011)_{\beta_I}$$

$$[11\bar{2}0]_{\alpha} \quad // \quad [1\bar{1}1]_{\beta_I}$$

(iv) Phase Transformation Sequences in Zirconium-Niobium and Zirconium-Tantalum Systems
(E.S.K.Menon, P. Mukhopadhyay, S. Banerjee and R. Krishnan)

Making use of computed free energy versus composition plots of the alpha and the beta phases in the binary monotectoid zirconium-niobium and zirconium-tantalum systems, the possible sequences of phase reactions in binary alloys of any given composition have been worked out.

In zirconium-rich alloys, where beta quenching leads to the martensitic transformation, the supersaturated martensite (denoted by α') decomposes during tempering through one of the following routes :

1. $\alpha' \longrightarrow \alpha + \beta_I \longrightarrow \alpha + \beta_{II}$, when the ageing temperature is lower than but close

to the monotectoid temperature (T_m) and the solute concentration, X, in the α' phase is less than X_o , the concentration at which the free energy curves for the alpha and the beta phases intersect.

2. $\alpha' \longrightarrow \beta \longrightarrow \alpha + \beta_I \longrightarrow \alpha + \beta_{II}$,

when the ageing temperature is lower than but close to T_m and X is greater than X_o.

3. $\alpha' \longrightarrow \alpha + \beta_{II}$,

when the ageing temperature is much below T_m.

In more concentrated alloys where the beta phase is stabilised, the decomposition of the beta phase follows one of the following sequences:

1. $\beta \longrightarrow \beta_I + \beta_{II}$,

when the ageing temperature is higher than T_m.

2. $\beta \longrightarrow \beta_I + \beta_{II} \longrightarrow \alpha^* + \beta_{II} \longrightarrow \alpha + \beta_{II}$,

when the ageing temperature is below T_m and in the range where the omega phase is unstable; α^* comes directly from β_I and contains much more solute than the equilibrium alpha phase.

3. $\beta \longrightarrow \beta_I + \beta_{II} \longrightarrow \omega + \beta_{II} \longrightarrow \alpha + \beta_{II}$,

when the ageing temperature is below T_m and is in the range where the omega phase is metastable.

The phase separation reaction $\beta \longrightarrow \beta_I + \beta_{II}$ could occur either through a spinodal mechanism or through a heterogeneous precipitation process, depending on whether the ageing treatment is carried out inside or outside the coherent spinodal.

3.2.2 Phase Transformations in Commercial Titanium Alloys

The influence of microstructure on the mechanical properties of several heat-treatable commercial titanium alloys has been studied with a view to examining the importance of different phase reactions in strengthening these alloys. Both $\alpha + \beta$

and β alloys have been selected for this work and the results obtained with some of these are summarised below.

(i) Precipitation of Widmanstatten Alpha in the Ti-6Al-2Sn-4Zr-6 Mo Alloy
(M. Mohan Rao and S. Banerjee)

It is known that several mechanical properties, particularly fracture toughness and tensile ductility, are strongly influenced by the shape of the alpha grains in $\alpha + \beta$ titanium alloys. In industrial practice, the control over the grain shape is achieved through a proper choice of the final fabrication step. When this temperature is in the beta region, the alpha phase precipitatesi in the form of Widmanstatten plates when the alloy is cooled after fabrication. On the other hand, when the finishing temperature lies in the $\alpha + \beta$ field, a distribution of equiaxed alpha and beta grains is produced. The mechanism of Widmanstatten alpha precipitation in the Ti-6Al-2Sn-4Zr-6Mo alloy has been studied here.

It has been found that a Widmanstatten alpha plate is made up of several finely divided alpha crystals, often twin related with each other. The twinning system has been observed to be of the $\{10\bar{1}2\}_{\alpha}$ type. Many of the alpha plates are constituted of a monolithic core enveloped by a layer of finely divided, contiguous alpha crystals having orientations that are approximately twin related with respect to that of the core. In the isothermally transformed samples, many instances have been found where the alpha crystals do not satisfy the Burger's orientation relation.

Quenching the alloy from the beta region produces an orthorhombic martensite which reverts back to the parent beta phase during electrolytic thinning of the quenched alloy. Samples quenched from the $\alpha + \beta$ field after allowing the separation of primary alpha have been found to consist of a mixture of the primary alpha and the orthorhombic martensite phases.

(ii) Effect of Heat Treatments on the Mechanical Properties of the Ti-8Al-1Mo-1V Alloy
(S.J.Vijayakar, S. Banerjee and R. Krishnan)

The influence of several heat treatment variables (e.g., solutionising temperature, duration and temperature of tempering after quenching) on the mechanical properties of the near alpha Ti-8Al-1Mo-1V alloy has been examined. The microstructures developed in the alloy after different heat treatments have been characterised by transmission electron microscopy and the changes in the mechanical properties have been correlated with the observed structures. Depending on the heat treatment conditions, various microstructural constituents like the primary α phase, the ordered α_2 phase, the martensitic α' phase, and the untransformed β phase with a fine dispersion of ω particles have been seen to be produced in this alloy. These constituent phases evolve through different types of phase reactions such as, Widmanstatten precipitation, ordering, martensitic reaction and omega transformation. The characteristics of each of these reactions, in relation to the Ti-8Al-1Mo-1V alloy have been studied.

It has been found that the primary alpha phase in the alloy, quenched from 750-850°C, undergoes a stress induced reorientation during deformation. This results in a considerable fragmentation of the alpha grains. These treatments correspond to relatively low values of yield stress and Young's modulus, suggesting that the stress induced reorientation occurs within the "apparent elastic deformation" of the samples tested. Solutionising in the low $\alpha+\beta$ region appears to be responsible for the attainment of a critical aluminium enrichment of the alpha phase so that this phase becomes susceptible to the stress induced reorientation process.

(iii) Influence of Omega and Alpha Precipitation on the Mechanical Properties of a Ti-15%Mo Alloy
(Uma Naik, G.E. Prasad and S. Banerjee)

The influence of the precipitation of the omega and the alpha phases on the flow and fracture behaviour of a Ti-15%Mo alloy has been examined. In this alloy the beta phase could be retained at room temperature in a metastable form on beta quenching. On subsequent ageing in the temperature range 300-700°C, the omega and the alpha phases precipitate at lower and higher temperatures respectively. The athermal omega phase is present even in the as-quenched alloy. Mechanical testing of samples containing either athermal or aged omega, in the range 250-350°C, shows a serrated flow behaviour, the average load drop corresponding to each serration and the critical plastic strain for the onset of serration being determined by the temperature of testing and the strain rate. In samples aged to form the equilibrium $\alpha+\beta$ structure, however, serrated flow is not observed during testing at the same temperatures. This implies that in this alloy, serrated flow is connected with omega precipitation during deformation at 250-350°C - a temperature range where omega formation is favoured.

The ductility of the alloy deteriorates drastically with the emergence of increasing amounts of the omega phase. A remarkable change in fracture morphology - from microvoid coalescence to cleavage fracture - accompanies this drop in ductility. It has also been noticed that extensive omega precipitation causes intergranular fracture with steps on the grain boundary facets.

3.2.3 Phase Transformations in Copper Alloys Precipitation

(i) Precipitation in Dilute Copper-Beryllium Alloys
(E.G. Baburaj, U.D. Kulkarni, E.S.K. Menon and R.Krishnan)

In view of the interest of the department in copper-beryllium alloys, the age hardening response of a binary Cu-1.77 wt%Be

and a ternary Cu-1.75wt% Be-0.6 wt%Co alloy has been examined in detail. Structural characterisation of these alloys in different heat treated conditions has been carried out using optical, X-ray and electron metallography. The influence of heat treatment variables on the mechanical properties of these alloys has also been investigated.

An examination of the sequence of precipitation in these alloys has shown that the emergence of the equilibrium CuBe phase (B2 structure) is preceded by a pre-precipitation phenomenon in which solute rich clusters are formed. The strains associated with such compositional fluctuations have been found to be reflected in the observed asymmetry in X-ray diffraction peaks and also in the appearance of a "tweed" contrast in electron micrographs. The streaking of electron diffraction spots along the $\langle 100 \rangle$ and the $\langle 110 \rangle$ directions in the reciprocal space has lent further support to this contention. X-ray diffraction has also shown the presence of a superlattice reflection which could be indexed as the $\{100\}$ peak of a beryllium rich metastable phase having the $L1_0$ structure. On progressive ageing this superlattice peak shifts gradually to the low angle side and finally attains the $\{100\}$ peak position of the equilibrium CuBe phase. From these observations it could be concluded that during ageing at low temperatures, precipitation occurred through the simultaneous operation of the continuous ordering and the spinodal clustering processes. This is accompanied by a gradual reduction of the axial ratio of the tetragonal unit cell to a final value of unity (corresponding to the equilibrium B2 structure).

With the addition of cobalt, the reaction has been found to be decelerated and thus it is easier to follow the sequence of the reaction in the ternary alloy. In addition, the

presence of cobalt in the alloy has been observed to restrict the grain growth during the solutionising treatment. This results in an enhancement in the strength of the ternary alloy vis-a-vis the binary alloy.

Correlation of microstructure and mechanical properties suggested that in these alloys the peak hardness and strength are associated with a microstructure consisting of a fine dispersion of CuBe (B2 structure) precipitates in the matrix. The pre-precipitation stages correspond to gradually increasing strength levels with increasing ageing time. The overageing process results in a growth of the precipitates and a consequent drop in the strength levels.

(ii) Precipitation in a Cu-8.82 Ni-6.12 Sn Alloy
(E.G. Baburaj, U.D. Kulkarni, E.S.K. Menon and S.Banerjee)

The precipitation sequence in a ternary Cu-8.82 Ni-6.12 Sn alloy has been investigated in view of the attractive combination of strength and ductility in this alloy. The decomposition of the supersaturated solid solution has been found to initiate through a spinodal mechanism. At a later stage of ageing discontinuous precipitation has been observed to occur and the resulting duplex cells have been seen to grow at the expense of the spinodally decomposed matrix. These cells are composed of the supersaturation-relieved alpha phase and an intermetallic $(Cu,Ni)_3Sn$ phase (DO_3 structure). The influence of these microstructures on the mechanical properties of the alloy has been examined. It has also been found that peak strength could be achieved here on ageing for very short periods.

3.2.4 Structural Characteristics of Intermetallic Phases with $L1_2$ and DO_{19} Structures
(E.S.K. Menon and P. Mukhopadhyay)

The hard sphere model, with its inherent assumption of

atomic incompressibility, is used extensively in describing crystal structures. However, it is believed that the applicability of this model is rather limited while dealing with metallic materials where the atoms appear to be readily compressible. The extent of validity of the assumption of incompressibility of atoms has been tested, in relation to the totality of the intermetallic phases having the $L1_2$ and the DO_{19} structures, by comparing the reported lattice parameters with those obtained on the basis of hard sphere model calculations.

In the case of the $L1_2$ phases, a plot of the calculated values (a') of the lattice parameter against the reported values (a) could be fitted to the straight line a' = 1.07a-0.25, which is very close to the ideal a' = a straight line in the region of interest. It has also been seen that for most of these phases the a' value lies well within ± 5% of the a value. It follows, therefore, that the atoms constituting these phases are not compressed much and that the description of the $L1_2$ structure in terms of a close packing of cannon ball atoms is not unreasonable. A similar conclusion has been arrived at with regard to the DO_{19} phases though the deviation from the hard sphere behaviour is somewhat more marked in this case.

The values of the space filling factor, in the case of the $L1_2$ phases, have been found to show a considerable scatter. However, both the arithmetic mean and the mode of the distribution lie between 0.75 and 0.80. This corresponds to a slightly better space filling than that obtained in the A_1 structure and points to a slight compression of the constituent atoms.

3.2.5 Texture Studies

(C.N. Rao and Lalit Kumar)

The effect of aluminium additions on the rolling structure of titanium has been examined. It has been found that the basal poles tend to orient closer to the normal direction

as the aluminium concentration increases.

Texture inhomogeneity in rolled zircaloy sheets has been studied with theaid of basal pole figures and normal axial pole figures obtained from different sections (from the top surface to the mid plane) of the sheets. The basal poles have been found to rotate towards the transverse direction in the surface layers indicating the presence of larger shear forces on the surface as compared to the interior during rolling.

An investigation on the anisotropy of thermal expansion and of yield strength in rolled zircaloy sheets is in progress. The results are being correlated to the texture in the material by using the axial pole figure. The method involves the evaluation of the BAPF by combining two or more pole figures which are obtained from x-ray diffraction data associated with three orthogonal surfaces. By appropriate stereographic transformations, the x-ray data are transformed to correspond to any desired set of reference directions and the resulting pole figures, in turn, are utilised to evaluate the texture density in the BAPF. This BAPF would directly yield the axial pole figure corresponding to the new normal direction. Thus the axes transformation for the BAPF is achieved indirectly by first transforming the x-ray data.

Fortran programmes based on this procedure have been developed for analysing the texture anisotropy in hexagonal materials.

3.2.6 Irradiation Induced Effects
(M. Sundararaman, S. Banerjee and R. Krishnan)

Irradiation induced void formation in alloys is strongly influenced by microstructure, the important microstructural parameters being the dislocation density and the nature, density and distribution of second phase precipitates. The effect of coherent

precipitates on void swelling has been examined using the generally accepted model of void formation which assumes that void embryos grow under a condition where equal number of vacancies and interstitials are continuously generated by the incident radiation but interstitials are preferentially absorbed in some sinks present in the material. The elastic strain fields associated with these coherent precipitates would interact with those due to vacancies and interstitials and this would result in the trapping of these defects. This elastic interaction has been evaluated for two specific types of coherency strain fields. It has been shown that the elastic interaction between the strain fields due to a precipitate and a point defect reduces to zero when the stress free strain associated with the precipitation process can be described as an isotropic dilatation. In such a situation there would not be any preferential attraction towards any specific type of point defect and thus the precipitate interfaces can be considered as variable biased sinks as has been assumed in the analysis due to Bullough and Brailsford. However, for other types of strain configurations, this assumption would not be valid.

3.2.7 Production of Ultrafine Metal Powders by the Freeze Drying Technique

(Lalit Kumar, V.K. Sasidharan, R.Krishnan and M.K.Asundi)

The freeze drying technique has been used for the production of ultrafine nickel powder. A fine stream of an aqueous solution of nickel formate is introduced into a cryogenic medium (e.g. liquid nitrogen) where it freezes in the form of small globules. These globules are separated from the cryogenic medium and are immediately dehydrated in the solid state under a dynamic vacuum at a suitable temperatures, taking care that melting does not occur during the process. The dehydrated residue consists of an amorphous aggregate of fine particles of the solute. The amorphous

nature of this aggregate has been established by X-ray diffraction. Decomposition of the dehydrated nickel formate is carried out at a suitable temperature (~ 280°C) in a hydrogen atmosphere to yield an ultrafine nickel powder, crystalline in nature. Electron microscopy has shown that these particles are spherical in shape and 800-1000A° in size. Efforts are being made to reduce the particle size further and to increase the yield of the metallic powder.

3.3 METAL PHYSICS

3.3.1 Solid State Diffusion - Metallic Systems

(B.D. Sharma, G.P. Tiwari, S.K. Khera, G.B. Kale, R.V. Patil, and V.V. Utgi)

(a) Self-diffusion in Dilute Zr-Fe and Zr-Cr Alloys

Self- and solute diffusion studies in dilute alloys are essential to understand the rate controlling diffusion mechanism. This is particularly important for the controversial case of diffusion in Zr alloys in b.c.c. phase. The temperature dependence of the self-diffusivity in a series of Zr-Fe and Zr-Cr alloys represented by Arrhenius relationship is listed below:

Table : 1 : Diffusion Parameters in β-Zr, Zr-Fe and Zr-Cr Alloys in 900-1250°C Temperature Range

Composition (at%)	Tracer	D_o, $M^2\ S^{-1}$	Q, KJ. Mol^{-1}
β-Zr	Zr^{95}	6.8×10^{-8}	145 ± 8
β-Zr	Fe^{59}	4.4×10^{-7}	116.95
Zr-0.98 Fe	Zr^{95}	6.33×10^{-7}	166 ± 8.2
Zr-1.35 Fe	Zr^{95}	2.08×10^{-7}	150.9 ± 13.4
Zr-1.64 Fe	Zr^{95}	1.62×10^{-7}	145.9 ± 7.2
Zr-3.54 Fe	Zr^{95}	2.9×10^{-7}	140.9 ± 7.2
Zr-6.37 Fe	Zr^{95}	5.16×10^{-5}	183.0 ± 10.0
Zr-2.0 Cr	Zr^{95}	5.16×10^{-7}	165.2 ± 7.5
Zr-3.5 Cr	Zr^{95}	2.05×10^{-6}	169 ± 8.7
Zr-4.1 Cr	Zr^{95}	1.39×10^{-6}	169 ± 4.5
Zr-7.86 Cr	Zr^{95}	1.59×10^{-6}	173 ± 2.6

The above diffusion data shows a negative value of correlation factor (-30.7 to -16.7) in 900-1200°C temperature range for diffusion of Fe^{59} in β -Zr. For the diffusion of Cr in β -Zr the correlation factor values is more reasonable. The implication of negative correlation factor is being examined on theoretical basis. This programme of tracer diffusion is being extended to other alloys of interest like Nb-Zr system.

(b) Chemical Diffusion in Multiphase Binary Systems

The kinetics of nucleation and growth of intermediate phases in multiphase binary couples are controlled by several factors such as interdiffusion coefficients, homogeneity range and heat of formation of the phases, crystal structures of adjacent phases, and their melting points etc. Evaluation of diffusion data is, however, intimately related to establishment of accurate concentration-penetration profiles by EPMA, identification of various phases, and analysis of concentration-penetration profiles in conformity to standard solutions. Interdiffusion studies on Fe-Ti and Th-Fe binary systems have been continued to understand the problems involved.

The concentration-penetration profiles of Fe-Ti couples diffusion annealed in 890-1050°C temperature range, are marked by absence of Fe-Ti and Fe_2Ti phases despite prolonged annealing. The temperature and composition dependence of interdiffusivity in titanium and iron-rich side of this system, can be written as,

$$\tilde{D}_{Fe\text{-}rich} = 2.2 \times 10^{2} \exp(-9.95\, C_{Ti}) \exp\left[\frac{-406-119C_{Ti}}{RT}\right], m^2 S^{-1}$$

$$\tilde{D}_{Ti\text{-}rich} = 5.39 \times 10^{5} \exp(-73.7\, C_{Fe}) \exp\left[\frac{-391-262\, C_{Fe}}{RT}\right], m^2 S^{-1}$$

where Q is in KJ/mol and C_{Ti}, C_{Fe} are concentration in at%. Absence of intermediate phases probably arises due to the relative flux of atoms moving across the phase boundary interface.

In the case of Th-Fe system, sandwich type diffusion couples have been annealed in 970-1040K temperature range and concentration-penetration profiles established by EPMA. These couples exhibited a time and temperature dependent growth of Th_7Fe_3 phase, and another one of a composition close to 50 at% The concentration profiles of diffusion zones showed that the latter phase grew at the expense of Th_7Fe_3 phase. As no near eutectic composition (45 at%Fe) intermetallic phase is reported in the phase diagram, the diffusion zone either represents a transient condition or characterises possibility of modification of phase diagram by lowering of eutectic temperature. The average diffusivities in the phases have been evaluated by applying Heumann's analysis and these can be represented by

$$D_{Fe\text{-}rich} = 3.07 \times 10^{15} \exp(-556/RT),\ m^2\ s^{-1}$$

$$D_{Th\text{-}rich} = 1.13 \times 10^{41} \exp(-1020/RT),\ m^2\ s^{-1}$$

where Q is expressed in KJ mol^{-1}. The diffusion couples also provided ample evidence of the brittle nature of diffusion zones. Work on several other points of interest is being continued.

(c) Interdiffusion in Binary and Ternary Solid Solutions

Interdiffusion problems in binary and ternary solid solutions besides the atomic mobilities of diffusing species is also controlled by vacancy winds effects. Because of this the diffusion of faster diffusing species is enhanced and that of slower ones is retarded. A programme to study interdiffusion and intrinsic diffusion coefficients in ternary solid solution of Fe-Cr-Ni system has been initiated. Suitable alloys for these studies have been melted - and it is proposed to investigate the composition dependence of diffusion profiles/paths as also the influence of vacancy behaviour.

The influence of 'vacancy wind' effect in diffusion kinetics of several solid solutions recently investigated e.g. Fe-Al, Ti-V, Fe-V systems etc., is also being re-examined.

Possibility of undertaking thermomigration studies in alloys of interest employing EPMA analytical techniques is also being planned.

3.3.2 Mass Transport in Nuclear Ceramic Oxides

(B.D.Sharma, D.D.Upadhyaya and S.V.K.Rao)

Mass transport in ceramic materials occurs through the migration of cation and anion vacancies, and the behaviour of these defects is the key to the understanding of the sintering mechanism. A programme of research pertaining to cation tracer diffusion, and chemical diffusion in mixed oxide system with emphasis on ThO_2 has been finalised, and will be taken up shortly.

3.3.3 Radiation Damage Studies
(B.D. Sharma, G.P. Tiwari, I.S. Batra and M.N. Vijayakumar)

(a) Diffusion Reactions during Post-Irradiation Studies

The annealing behaviour of neutron irradiated zircaloy-2, nickel-titanium alloys etc. has been investigated in the past, using changes in the strength parameters. These changes are not sensitive to point defects and the diffusion reactions arising due to migration of these defects. Presently, a programme to establish a post-irradiation laboratory with capability of handling resistivity measurements upto liquid He temperatures is in the planning stage. In the meantime, initial work on nickel alloy making, specimen fabrication and specially designed specimen holders etc. is in progress. It is also proposed to employ positron annihilation techniques for this kind of investigations.

(b) Mechanical Properties of Neutron Irradiated Hard hcp Metals and Alloys

Radiation hardening studies on hard hcp metals and alloys have been continued. A series of investigations on neutron-irradiated commercial α -titanium has been completed. Sheet specimens of sponge purity titanium (oxygen content $\sim$ 1400 ppm) in α -annealed condition with an average grain size of 20μ were neutron irradiated in APSARA reactor to different integrated flux levels. Both annealed and neutron-irradiated specimens were tensile tested to examine the strain rate sensitivity in 77-373K temperature range and also to determine the internal stress by the stress-relaxation technique.

Present studies on hard hcp metals Zr and Ti, have confirmed the rate controlling deformation mechanism to be due to Peirels and Nabarro below 200 K, and probably cross glide at higher temperatures. Neutron irradiation of these metals of low interstitial content did not alter the low temperature mechanism, but, at higher temperatures, increased defect-dislocation interactions were observed. Yield point phenomenon and work-hardening characteristics of these metals could be rationalized in terms of dislocation dynamics. In the case of commercial purity metals, interstitial oxygen-dislocation interaction remained the rate controlling mechanism in the whole temperature range of 77-373K. Neutron irradiation did not cause any changes in the rate controlling process.

(c) Radiation Hardening Studies in fcc/bcc Alloys

The irradiation - physical and mechanical property correlation in several fcc and bcc solid solutions and two phase alloys is of interest because of their likely application in different kind of nuclear reactor systems. Of particular interest in this category are some nickel, aluminium and niobium base alloys. In continuation of the earlier studies on Nickel-Titanium alloy, a programme to study

solid solution and irradiation strengthening effects in Ni-V and Nb-Zr alloys are being initiated. Literature survey has indicated reduced radiation swelling in the two phase Ni-V alloys and also probability of substantial microstructural changes during long term neutron irradiation of Nb-Zr alloys due to transmutation processes. Irradiation induced diffusion reactions in unsaturated solid solutions lying close to a two phase boundary can also result in the nucleation of precipitates. At present stage, appropriate alloy compositions, which will be realistic to irradiation induced effects are being finalised and are being taken up for melting and fabrication.

3.3.4 Studies of Inert Gases in Metals (G.P. Tiwari and K.C. Paliwal)

Inert gas behaviour in metallic systems is of relevance to structure-property correlation. Currently, two aspects, i.e. (i) nucleation and growth of helium gas bubbles in copper-boron alloys subjected to neutron irradiation, and (ii) gas release from these alloys during isochronel/isothermal annealing, have been in progress. The role of spontaneous vacancy condensation on gas bubbles contributing to their growth, and consequently to swelling problem has been examined by forming binary diffusion couples of irradiated (Cu + B) alloy and nickel. The vacancy drift due to differential atomic mobilities of Cu and Ni atoms, is found to influence growth of gas bubbles in the diffusion zones. Evidence to show enhanced nucleation and growth of bubbles in the vicinity of free surfaces - suggests that such surfaces act as sources of vacancies which take part in the nucleation of helium gas bubbles.

The data concerning gas release from irradiated Cu-B alloys - annealed to different durations in 400-1050°C temperature range, is being examined to arrive at quantitative conclusions.

A programme to investigate the mechanical properties of inert gas doped metals is also being planned employing suitable nuclear reactions, and would be taken for detailed investigations in the coming year.

3.3.5 Splat Cooling Studies

(P.K.K. Nayar)

Studies on splat cooled metals and alloys have revealed that the microstructure of the matrix in these cases is dependent on both the temperature of the melt and the substrate - besides the substrate material. This is due to the fact that in liquid quenching, the nearest neighbour configuration of atoms in the liquid state itself provides the nucleation sites. Diffusion reactions in splat cooled alloys do not exhibit enhanced diffusion effects - as the free vacancies are usually 'agglomerated' into relatively stable structures. In a recent investigation on Al-3.7%Cu alloy splat cooled from 900°C to liquid nitrogen temperature, the transformation kinetics of θ phase formation has been examined. Following resistivity techniques. Ageing of splat cooled alloy films (20 μ thick) at 175, 200, 250 and 300°C provided resistivity data which could be expressed by the usual fraction transformed-time relationship, i.e.

$$f = 1-\exp \left[1-(K.t)^{n} \right]$$

where K and n are the reaction constant and exponent respectively. The analysis of the data led to linear log ln $(1-f)^{-1}$ vs log t plots with reaction exponent n = 1.46. Activation energy determined taking into account the incubation period for 0.1% phase transformation, corresponded to a value of 26.6 Kcal/mole. This is comparable to diffusion activation energy of Cu with Al lattice. This suggests that short range diffusion of Cu atoms is probably responsible for nucleation of θ phase in this type of materials. Investigation on Al-Sn and Al-Si alloys is also in progress.

3.3.6 INSTRUMENTATION

(P.K.K. Nayar and R.V. Patil)

(a) A system for flash heating and rapid quenching of metals and alloys by employing condenser discharge pulse in the range of 10^4 amp at 50 volts D.C. has been assembled. The system provides for a heating rate of 10^7K/sec. for 25 μ thick foils, and a quenching rate of $\simeq 10^5$K/sec. The system has applications in splat cooling, preparation of fine grained structure, and study of different kinds of transformations.

(b) A low background, high resolution X-ray diffractometer using Cu K_{α_1}, radiation, double crystal monochromator, and double crystal analyser has been designed to scan the range $-7° < 2\theta < 90°$. The design provides for a temperature control in 77 to 600 K range. The engineering designs of the apparatus are being prepared at this stage.

(c) A preliminary survey to set up a R.F. or D.C. sputtering/etching unit for diffusion studies has been made, and effort would be made to set up this facility during the coming year.

3.3.7 Progress on R-5 Irradiation Facilities

(a) Planning

(B.D. Sharma)

A report on Radiation Damage; Present status and future perspectives- signifying the areas of current and future interests with respect to both from basic and applied research points of views has been prepared. The role of advanced research techniques for post-irradiation research of different kinds has been individually reviewed. R-5 irradiation facilities must be supported by adequate post-irradiation research laboratories with capabilities of handling cryogenic experiments. Formation of several groups to undertake and set up a tradition in resistivity and X-ray studies of irradiated

samples, positron-annihilation studies, cyclotron irradiation and related problems is planned. Initial work on organising this activity has already been initiated - to begin with by looking into procurement of high sensitivity equipment for resistivity studies of point defects in metallic systems.

(b) Low Temperature Irradiation Facility
(B.D.Sharma, P.K.K. Nayar, S.K. Khera and G.P.Tiwari)

A tentative design for R-5 low temperature irradiation facility - providing for variable irradiation temperature control of 20K and above, and facility for removal of irradiated specimens, has been designed. It is proposed to employ compact cryogenerators with cold helium gas as coolant for irradiation capsules. To convert this tentative design to drawing reality, numerous problems concerning cryogenics, heat loads - both nuclear and conventional, radiation streaming and protection therefrom, cryocapsule design and guidance system etc. are being considered. Optimisation of heat load, and radiation protection are critical areas in designing such equipments, and careful evaluation is essential, and would be undertaken.

(c) In-pile Creep/Corrosion Experiments

These experiments are in initial stages of planning.

4. CORROSION AND ELECTROMETALLURGY

The activity of this section comprises of research and development work in the fields of corrosion and electrometallurgy. A good number of research programmes is inter disciplinary in nature.

The corrosion group has continued its activities in studying the high temperature corrosion behaviour of various materials of interest to nuclear programmes, corrosion rates of various materials in sea and salt water applications and stress corrosion cracking of austenitic steels nickel base alloys and zirconium alloys.

The electrometallurgy group has been engaged in studies on electroplating of metals, alloys and composites, electroforming of meshed products, electrowinning of copper and nickel by fluidized bed electrolysis and electrophoretic deposition of graphite and nickel oxide as well as studies on packed bed electrodes and electrowinning of rare earth metals.

The section is also engaged in offering consultancy services to the different units of DAE in solving various corrosion problems in different plants, rendering advice in materials selection and supplying electroplated components.

4.1 HIGH TEMPERATURE CORROSION AND OXIDATION STUDIES

4.1.1. Zirconium alloy development:

a) Corrosion tests on the experimental Zr-0.5 Nb - 1 Cr alloy (H.S. Gadiyar)

In the zirconium alloy development programme, several binary and ternary alloys based on Nb and Cr additions have been corrosion tested to compare their behaviour with that observed with zircaloy -2. The experimental alloy Zr - 0.5 Nb - 1 Cr was found to have corrosion rates comparable to that of zircaloy - 2 in high purity, high temperature (upto 360°C) water and the rates were much lower in high temperature

(400-550°C) steam, with added advantage of lower hydrogen adsorption than zircaloy-2 under out of pile conditions. Steam corrosion tests on this alloy have been continued.

The 3 and 14 day AECL specification tests in steam at 400°C (1500 psi) were carried out. Two other experimental alloys, namely Zr - 0.3 Fe - 1 Cr and Zr - 0.3 Fe - 1 Cu were also included in this test. The weight gains obtained were considerably below the AECL specified values of 22 and 38 mg/dm^2 indicating their satisfactory corrosion resistance. Amongst the three alloys tested, Zr - 0.3 Fe - 1 Cr showed the lowest weight gain.

b) Effect of Al, Mn and N_2 as impurities in zircaloy - 2 on its corrosion resistance.

(H.S. Gadiyar)

The 3 and 14 day tests carried out on several zircaloy - 2 specimens with varying amounts of Al as impurity has shown that Al contents upto 140 ppm have no significant effect on the corrosion rates of zircaloy - 2. This has been arrived at also by analysing the data from several such studies reported in the literature. As regards impurity limits for N_2 and Mn, analysis of the data has not shown any detrimental effect upto 118 and 290 ppm respective additions. The maximum specified limits of Al, N_2 and Mn in zircaloy - 2 are 75, 80 and 50 ppm respectively.

4.1.2. Effect of prefilm on the corrosion of zircaloy - 2 in high temperature water

(S.V. Phadnis, K.B. Gaonkar and H.S. Gadiyar)

Studies on the corrosion of zircaloy - 2 in 350°C double distilled water at saturation pressure (2300 psi) have been continued in the presence of prefilms formed under different experimental conditions. The prefilming conditions were :- i) steam at 400°C, 1500 psi ii) water at 300°C, 1100 psi iii) oxygen at 600°C, 1 atmosphere. Prefilm thickness is about 1 micron. Prefilming in water

at 300°C was found to give weight gains initially, upto a period of 25 days. However, continued exposure upto 120 days have resulted in lower weight gains for specimens prefilmed in oxygen. Average weight gains of 45.6, 47.8, 58.6 mg/dm^2 were observed for specimens prefilmed in O_2, steam and water respectively after 120 days of exposure. Further long term exposure to observe the extent of hydrogen absorption on the coupons under these conditions is in progress.

4.1.3 Effect of surface chloride contamination on the high temperature oxidation of Zircaloy - 2.
(K. Elayaperumal, H.S. Gadiyar and S.V. Phadnis)

Studies have been initiated to see the effect of surface chloride contamination on the high temperature oxidation of Zircaloy-2 and also to see the effect of imposing an external stress on the specimen. The salt contamination was effected by dipping the specimens in a solution of 1% NaCl, then drying in air to give a salt coating of 16 mg/cm^2. Such chloride contamination enhanced the oxidation rates at 600°C in flowing oxygen by about 50% over that of uncoated specimens. Both stressing by U-bent and also by uniaxial tensile testing (at a stress level of 20 Kg/mm^2) have not resulted in visible cracking at a temperature of 350°C for a period of 72 hours.

4.1.4 Corrosion of carbon steel in high temperature water. Effect of dissolved oxygen and EDTA additions.
(S. Chakravarty and H.S. Gadiyar)

It was earlier reported that the growth rate of carbon steel in lithiated water of pH 10.5 at 310°C can be considerably reduced by reducing the dissolved oxygen to less than 0.1 ppm. The study has been extended for longer periodsand also in water of pH 7.0. On examining the surface both by x-ray and SEM, magnetite, (Fe_3O_4), was found to be the main constituent of the oxide. At pH 7.0, an initially high percentage of Fe_2O_3 (15 to 20% after six days) was found. This has almost completely converted to the protective magnetite after about 20 days of exposure. The SEM examination has

shown two layer oxide growth, a thin finely crystalline randomly oriented base film, and over than uniform well defined much larger crystallites both consisting of magnetite. The adherence and protectiveness of this magnetite coating was found to improve by the addition of 300 ppm of sodium salt of EDTA. This has resulted in very low corrosion product release rate (0.72 mdd after 22 days). Further studies with regard to composition and adherence of this coating with addition agents on longer exposure are being continued.

b) Electrochemical measurements.

The electrochemical measurements on plain carbon steel and on carbon steel with a magnetite layer were carried out in 1M LiOH. The potential-time curves indicated the attainment of a stable passivity for both the cases in deoxygenated water. In another experiment, the plain carbon steel was cathodically treated to obtain the film free surface, and on obtaining a complete anodic polarization curve, two negative loops were distinctly seen, indicating the solubility of the initial lower oxide films, before the build up of a passive layer. This passive layer has been identified to be Fe_3O_4 of thickness about 40A° from Ellipsometric measurements.

4.1.5 Ellipsometric study of surface films on metals.
(S. Chakravarthy and H.S. Gadiyar)

The ellipsometer, model L-119 from M/s Gaertner Scientific Corporation, has been commissioned to initiate studies on the characterisation of thin surface films on metals. A beam of polarised light on reflection from a surface causes a change in the relative phase of the 'P' and 's' components and a change in the ratio of their amplitudes. Measurements of these differences accurately with the ellipsometer leads to the determination of n, the refractive index and K, the absorption coefficient of the material. The instrument has been aligned and initial measurements during standardization using a standard glass plate has given a value of n = 1.480, while the absolute value is 1.516. A carbon steel specimen showed n = 2.381 with air-formed oxide film, n = 2.594 with an oxide formed in 1 M

LiOH for 24 hours and n - 2.991 after cathodic reduction of the latter oxide film. The reported values of n for pure iron are between 2.90 and 3.30.

An in-situ cell is being designed at present to study the anodic oxide films on Zr and on steel in 1 M LiOH.

4.2 STRESS CORROSION CRACKING

4.2.1 Microstructural effects on SCC of zirconium base alloys. (G.C. Palit and K. Elayaperumal)

Present investigation is intended to reveal the structure sensitive SCC susceptibility of various zirconium base alloys in methanol - 0.4% HCl solution. The alloys studied were Zr-1% Cr, Zr-2% Fe, Zr-2% Cu and Zircaloy - 2. All these alloys are susceptible to intergranular stress corrosion cracking in alpha annealed condition. Spherodisation treatment, i.e. prolonged annealing in the α-phase range, induces more susceptibility to SCC in these alloys. The alloys are highly susceptible to transgranular SCC in the β-quenched martensitic form. Further tempering improves SCC resistance: tempering for 24 hours at 700°C ensures complete immunity to SCC in Zr-2% Cr alloy, due to continuous net work of intermetallic compound at prior β- grain boundaries. Similar tempering treatment in Zr-2% Cr also induces immunity to SCC, but such net work is not observed, even after ageing for a long time (80hours) at 700°C. Tempering for 8 hours at 700°C show optimum resistance to SCC in Zr-1% Cr alloy, but not complete immunity. Tempered martensitic structure has no significant effect on SCC resistance of Zr-2% Fe andZircaloy - 2.

Annealing in the $\alpha+\beta$ phase regions ensures complete immunity to SCC in Zr - 2% Cr alloy, attributed to the presence of duplex eutectoid structure at the grain-boundaries. Similar treatment has no beneficial effect on Zr - 1% Cr. Such treatment shows pearlitic lamellar structure at the equiaxed α grain boundaries in Zr - 2% Fe without any improvement in SCC resistance. Zr - 2% Cu does not show any susceptibility.

When furnace cooled from the β-phase region all the binary alloys show Widmanstattan structure due to precipitation of platelets α surrounded by pearlitic eutectoid. Stress corrosion crack is observed to propogate along α-plate duplex eutoctoid boundary in Zr-1% Cr and Zr-2% Fe. Further work is in progress to correlate SCC susceptibility with respect to mode of crack propogation, micrestructure and alloy composition.

4.2.2 Iodine SCC of Zircaloy - 2.

(K. Elayaperumal, P.K. De and S.K. Ghosal)

The earlier work carried out with stressed zircaloy rings exposed to iodine vapour at 300°C has not resulted in SCC. A new experimental assembly has been fabricated for testing zircaloy fuel tubes for SCC by pressure burst technique in the presence of iodine.

RAPP - type Zircaloy - 2 fuel tubes were tested in the as-received condition with graphite coating in the inside surface and also with pre-hydriding in pure hydrogen. Stress corrosion testing was done at temperatures of 300 to 400°C with applied hoop stress varying from 27 to 33 Kg/mm^2 under the above condition. Iodine concentration was varied from 1 mg/cm^2 to 10 mg/cm^2.

Testing at 400°C with 10 mg/cm^2 of iodine has resulted in failure in a very short time, as low as 7 minutes, whereas testing at same temperature with 1 mg/cm^2 of iodine resulted in a failure time of 10 hrs. Results of the further tests with 1 mg/cm^2 of iodine indicate that the time to failure decreases from 190 hours to 10 hours as the temperature of test increases from 300 to 400°C. For cracking to occur the applied hoop stress should be around the yield stress of the tube (y.s. at 300°C = 30.8 mg/mm^2). Graphite coated tube did not fail for 240 hrs. at 400°C whereas the as received tube failed in 10 hours under similar condition. In the absence of iodine small amounts of H_2 (40 ppm) has no effect on the SCC susceptibility.

SEM examination showed considerable corrosion product at the inside surface of the tube. No cracking was observed in the absence of iodine.

4.2.3 Stress corrosion cracking of Heat Exchanger tube materials in high temperature water
(P.K. De and S.K. Ghosal)

Stress corrosion cracking of common heat exchanger materials, AISI 304 and 304L stainless steels, Inconel 600, Incoloy-800 and Monel-400, has been studied in high temperature water at 315°C and 1500 psi. The testing has been done with U-bend specimens. Load was added to water as impurity since ASME Boiler and Pressure Vessel code cautions against the presence of lead compounds at temperatures above 204°C. Lead was varied from zero to 300 ppm, while oxygen ranged from <50 ppb to 8 ppm. The room temperature pH of the water was controlled at 9.6. The exposure period was 1600 hours maximum. The materials were tested in various metallurgical conditions: mill annealed, cold worked and cold worked plus stress releived. Results indicate that type 304L stainless steel, Incoloy-800 and Monel-400, irrespective of the previous heat treatments, are resistant to cracking. Inconel-600, whether it was mill annealed, cold worked or stress releived, failed by stress corrosion in all tested conditions. Severe cracking was observed in cold worked (25%) type 304 stainless steel specimens in environments irrespective of the presence of Pb and O_2. Shallow cracks were found in some mill annealed 304 stainless steel specimens. Cold worked plus stress releived specimens of 304 stainless steel did not fail in any of the environments.

Microscopicexamination of the failed Inconel-600 specimens showed a mixed intergranular and transgranular mode of cracking, whereas 304 stainless steel showed transgranular cracking.

4.3 CORROSION IN SALT WATER AND HALIDE SOLUTIONS.

4.3.1 Corrosion of Titanium, Cu-Ni and Ni base alloys in flowing sea water.
(P.R. Shibad).

The Cu-Ni alloys, In 838 and In848 and pure titanium were exposed to sea water at CIRUS Jetty at a flow velocity of 2.4 meters/sec for a total period of 340 days. It is observed that alloy In848 is better corrosion resistant than alloy In838 (the mg/dm^2 values for In848 and In838 are 630 and 1415 respectively). Titanium is found to be unaffected in the above conditions.

4.3.2 Galvanic corrosion of carbon steel in salt water (K. Elayaperumal, S.S. Chouthai and P.R. Shibad)

Galvanic corrosion experiments mild steel has been studied using aluminium brass as cathode in fresh tap water and synthetic sea water, stirred at 50 r.p.m, for 1 day using a mixed cathodic inhibitor of $ZnSO_4$, $7H_2O + HSO_3NH_2 + NaH_2PO_4$ at 6 and 60 ppm concentration.

It was observed that even though corrosion rate increases with reduction in area of mild steel (ratio of mild steel to Al brass varied from 1.06 upto 0.01) in both tap water and in synthetic sea water,the inhibitor effeciency is 99% for all the area ratios studied in tap water. In synthetic sea water also the inhibitor effeciency increases with reduction in mild steel area. However, 60 ppm inhibitor concentration shows better results than 6ppm. The efficiency is however less than that observed in the case of tap water.

4.4. CORROSION STUDIES IN VARIOUS ENVIRONMENTS
Corrosion of Hastelloy-X in acids
(P.R. Shibad)

In connection with a request from a fertiliser industry for evaluation of corrosion rates of materials of construction for phosphoric acid manufacture, the following programme has been carried out. It consists of testing passive materials like Nickel, Monel, Inconel and some Hastelloys in the filtrate of rock phosphate treated with H_2SO_4 and also in straight acids like HCL, HNO_3 and H_3PO_4. Preliminary tests indicated Hastelloy-X to be better than the rest of the materials. Detailed further investigations were carried out with Hastelloy-X. The tests were carried out at different concentrations

The tests were carried out at different concentrations and temperatures. The effects of metallurgical conditions of the alloy on intergranular corrosion in standard Strauss solutions were also studied.

It was observed that the corrosion rates are generally low and within the acceptable value of 5 to 50 mpy (0.125 to 1.25 mm/yr). The rates in concentrated HCl and in other acids at elevated temperatures are close to the higher limit of acceptance. It was also observed that this alloy does not get sensitized even after long heat treatment at the normal sensitizing temperatures of 600 - 900°C. These treatments have not resulted in high corrosion rates.

4.4.2 Corrosion studies of aluminium base alloys in HCl with and without organic inhibitors
(P.R. Shibad and K.N. Adhe)

Experiments were carried out on Al - 0.7% Be and Al - 0.2% misch metal alloys in 1N HCl with varying concentration of acridine (upto 1 gm/litre) as inhibitor. A simple model of adsorption is found to be satisfied by making use of the relation log $\theta/1-\theta$ versus log C, where θ = surface coverage, C = concentration of the inhibitor in molality. The results obtained are in reasonable aggrement with the Langmuir adsorption isotherm. For the two alloys the inhibitor effeciencies are well over 78% in 1N HCl.

4.4.3 Corrosion behaviour of wrought and electrodeposited nickel in alkaline environments - effect of NH_3, S^-, and Cl^-.
(K. Elayaperumal, P.K. De and S.K. Ghosal)

Corrosion behaviour of wrought Ni and electro-deposited Ni (ED-Ni) in KOH solutions at 25°C with or without contaminants like NH_3, H_2S and Cl^- has been studied by potentiostatic anodic polarization, current decay behaviour at controlled potentials and by weight loss techniques. Results showed that corrosion rate of both wrought

Ni and ED-Ni in 6M KOH solution was negligible. Passive current density for ED-Ni wasof the order of 10^{-5} amp/cm^2, 100 to 200 times higher than that of wrought Ni. With the additions of NH_3, H_2S and Cl^- in 6M KOH solutions, the corros ion rate of ED-Ni was greatly enhanced and was in the range of 40 to 100 mdd. Corrosion rate of wrought N_1 was marginally increased to 0.23 mdd in only Cl^--containing KOH solution while no appreciable weight loss was observed in 6M KOH solution containing either NH_3 or H_2S. In these solutions the corrosion potential for both wrought Ni and ED-Ni became more active. Passive current was unaffected by addition of NH_3 or Cl^-, but increased to 10^{-3} amp/cm^2 by the addition of H_2S. The lower corrosion resistance of ED-Ni, particularly in the presence of contaminants, is explained in terms of sulphur pick up during plating.

4.5. ELECTROPLATING OF ALLOYS AND COMPOSITES

4.5.1 Electro deposition on Nickel - Manganese alloys (A.K. Grover and John T. John)

Continuing the programme on the electro deposition of alloys, studies have been made to electrodeposit wear and oxidation resistant nickel manganese alloys from metal chlorides contained in dimethyl sulphoxide-water mixture bath. The effect of various parameters like pH, temperature and current density (C.D) on the composition and quality of deposits was studied from 80 mole% Mn-20 Mole% Ni bath. Studies have shown that smooth, bright, thin coatings of nickel-manganese alloys containing 10 to 90 wt% Mn can be deposited from 80 mole% bath by adjusting the plating parameters.

Not much change in deposit composition was observed with change in bath composition from 30 mole% Mn to 60 mole% Mn. Studies conducted from 30 and 60 mole% Mn bath to establish the role of ammonium chloride addition showed that it does not affect to any appreciable extent the composition of the deposit. However, it improves the bath conductivity and 1.0 to 1.5 M NH_4Cl is necessary

to get good quality deposits. In general, increase of C.D and decrease in bath temperature decrease the manganese content of the alloy for all the baths studied. Current effeciency of alloy deposition showed a slight upward trend with increase in bath temperature.

The optimum bath conditions to obtain a smooth, adherent and shining alloy deposits from DMSO - water mixture bath are as follows:- 20-80 mole% Mn, Ni + Mn 1-1.5 M., ammonium chloride 1M, 5V% DMSO, 50 gpl glycine, pH = 3, 50°C temperature and cathode current density of 4-40 A/dm^2.

4.5.2 Photo fabrication of porous nickel tubes
(A.K. Grover and John T. John)

Studies were carried out to standardise the conditions to electroform porous nickel tubes using photofabrication technique. Aluminium wasused as expendable mandrel. After cleaning and drying the mandrel, it was coated with a photoresist and exposed to ultraviolet radiation through a negative transparency having the desired pattern. Exposure and development process was standardised to get a good quality pattern on the aluminium surface. Plating was done from nickel sulphamate bath. S-Nickel shots were used as anode. In the present study, patterns of 330, 540 and 1060 microns were used. A series of electroforming experiments were conducted for varying time depending upon current density and the starting pore size of pattern. It was possible to electroform good quality porous nickel tubes 4-5 mil, 7-8.5 mil and 7 mil thick using 330, 540 and 1060 microns pattern respectively. As the thickness of electroform was increased, the holes started closing. The maximum thickness of tube is limited due to tapering overgrowth of metal within holes.

In order to achieve greater tube thicknesses, the plating was carried out in two stages. Resist coated mandrel was exposed for 15

minutes as thicker resist coating was applied. After getting the proper pattern on the mandrel, it was plated 13.5 A/dm^2 to give 1.5-2 mil thick nickel deposit. Aluminium mandrel was then dissolved in alkali, followed by acid treatment of the nickel mesh. Porous nickel tube is further plated at the same current density. It was possible to electroform thicker porous nickel tubes. Porous nickel tubes of 7-8 mil, 9.5-10 mil and 20 mil thickness could be electroformed using this two stage technique with 330, 540 and 1060 micron patterns respectively.

The nickel electroformed from this bath has microhardness 280, tensile strength 64 Kg/mm^2 and 5.4% elongation. Tensile strength of nickel decreased to 18.5 Kg/mm^2 and elongation increased to 37.1% on annealing in vacuum at 750°C for 90 minutes.

4.5.3 Electroplating of refractory metals
(Sohan Singh, A.K. Grover and A.L. Pappachan)

Work on fused salt electroplating of various refractory metals of interest like zirconium, tantalum etc., which cannot be electroplated from aqueous bath, was taken up. Studies were initiated to electroplate coherent deposit of zirconium from fused salt bath using zircaloy-2 scrap as anode. The bath consists of 16.3 wt.% K_2ZrF_6 in a ternary eutectic of LiF-KF-NaF. Purified argon gas passed through the system during electrolysis. 12 mm and 16 mm dia copper rods were used as cathodes. A few experiments were conducted at 750°C-800°C, at cathode current density of 2A/dm^2 for 3-4 hours. In the preliminary experiments either non uniform metallic coating or only a flash coating was obtained. Qualitative spectroscopic analysis of the metallic coatings confirmed the presence of Zirconium metal.

4.5.4 Electrodeposition of Ni/NiO composites
(M.N. Joshi and M. Totlani)

Ni-NiO composites have potential applications in M.H.D. Programmes. Studies have been initiated to co-deposit NiO with nickel. NiO in the bath has been varied from 25 gpl to 125 gpl. The deposition has been carried out at 35 A/dm^2 for four hours, the temperature and pH being 55-58°C and 4 respectively.

It was possible to obtain smooth electroplates of Ni/NiO composites containing a maximum of 5% NiO from a bath containing 125 gpl of NiO. The ductility of deposits decreases with the amount of NiO in the deposit. After heat treatment at 350°C for 1 hour in vacuum, the plates showed considerable ductility.

4.6 ELECTROPHORETIC DEPOSITION

4.6.1 Electrophoretic deposition of nickel oxide
(K. Elayaperumal, M. Totlani and A. Ramasamy)

The work on electrophoretic deposition of green nickel oxide has been continued with n-butanol and trichloroethylene mixture as the suspension medium. Parameters affecting the deposition rate at room temperature such as concentration of nickel oxide in the suspension, composition of the suspension medium, applied voltage and deposition time have been studied in detail.

It was observed that with the increase in nickel oxide concentration in the bath upto 75 gpl, the rate of deposition increases and beyond this concentration it remains practically constant. Deposition would not be achieved from either pure n-butanol or pure trichloroethylene bath. A minimum of around 15 vol.% trichloroethylene was essential to get a uniform deposit. With further increase of trichloroethylene, the rate of deposition passes through a maximum and deposition ceases after a concentration of about 55 vol%. Rate of deposition increases linearly with applied voltage and time of deposition in the range 100-400V and 15-240 seconds respectively.

4.7 ELECTROWINNING OF RARE-EARTH METALS

4.7.1 Electrowinning of Lanthanum
(Sohan Singh and A.L. Pappachan)

Work on preparation of pure lanthanum from lanthanum chloride in NaCl-KCl bath was carried out. In an electrolytic cell having 40 wt.%

$LaCl_3$ in NaCl-KCl as charge, experiments were conducted at 960-970°C with molybdenum cathode and graphite container as anode. For short duration, a current effeciency as high as 95% was achieved. The current effeciency was found to be highest at a cathode current density of 7.5 Amp/cm^2. The maximum yield was 88% when the amount of ampere-hour passed was 50% more than the theoretical amount required for complete deposition of lanthanum. It was observed that current effeciency falls down rapidly, when the concentration of $LaCl_3$ in the melt comes down to less than 20 wt%.

4.7.2 Preparation of Cobalt-Cerium alloy
(Sohan Singh and A.L. Pappachan)

The work on getting cobalt-cerium alloy for making permanent magnets was continued. The alloy was prepared by various methods mentioned in the earlier report. It was found on analysis that there is a loss of cerium during the induction melting. To get the right composition ($CeCo_5$) of the alloy, 2% excess cerium was taken over the stochiometric amount. The alloy was crushed to a fine powder and the average diameter of the particle was found to be 6.9 μ by Fisher Sub Sieve Sizer method. The coercivity was found to be over 300 Oe in an applied field of 4 KOe. Further work is in progress to improve the magnetic properties of the alloy.

4.8 ELECTROWINNING OF METALS USING PARTICULATE BED CATHODES

4.8.1 Electrowinning of Ni from dilute $NiSO_4$ solution
(M. Totlani and P.R. Singh)

The study of electrowinning of Ni from dilute $NiSO_4$ solution on to a particulate bed of Ni has been continued. Effects of various parameters like temperature, electrolyte flow rate, concentration of Ni in the electrolyte cell, current and pH of the feed on the cathode current effeciency for Ni deposition were studied.

Effeciency was found to increase with temperature, Ni concentration and pH of feed solution appreciably. It varies linearly

with Ni concentration in the feed between 1 to 3.5 gpl. Effect of pH of feed was very marked. At pH 1.35 it was less than 10% while at pH 5.0 it was around 44.6%. The effeciency increased with cell current initially and then saturated at around 600 ma. The effect of increase in bed height from 1.1 cm to 1.8 cm was not appreciable.

4.8.2 Packed bed electrodes
(M. Totlani and P.R. Singh)

Study on packed bed graphite electrodes has been taken up to treat very dilute solutions. The system studied is $CuSO_4$-H_2SO_4.

The preliminary cell was made of 1.2 cm bed of graphite particles (+20, -7 mesh) in ~3.1 cm (i.d.) glass tube. A nickel mesh was used to feed current. Anode was under gravity maintaining aconstant column over the sintered glass disc, fused to support the bed. Two concentrations of Cu, i.e. $5X10^{-3}$M and $1X10^{-3}$M in 1M H_2SO_4 were used. It has been found that the limiting current for Cu deposition increases with copper concentration in the electrolyte and the electrolyte flow.

4.9 INTER SECTIONAL/DIVISIONAL PROGRAMMES

4.9.1 Collapse and ridging behaviour of RAPP fuel pins
(P.K. De)

A programme has been undertaken in collaboration with PPED, RED and RMS to study the effect of yield strength and pellet-clad gap on the collapsing and ridging behaviour of RAPP fuel pins. Half length fuel pins of RAPP type, with yield strength varying from 49000 psi to 58000 psi and the pallet clad gap varying from 0.003" to 0.008" were tested in autoclaves at temperatures ranging from 315°C to 500°C and pressure from 800 psi to 1500 psi. The ridges and ovality formation were measured by a profilometer. With testing at 315°C, 1500 psi for 20 hours, the largest ovality changes about 100μ have been observed in elements which had the largest diametral gap, irrespective of the yield strength.

Circumferential ridges of maximum 60μ were obtained in the temperature range of 400°C to 500°C and 1500 psi. The formation of ridges seems to be independent of the cladding yield strength or diametral clearance in the element in the temperature range of 350 to 500°C. The circumferential ridge formation appeared to be strongly dependent on the temperature beyond 350°C. Based on these experiments, recommendations were made regarding the pallet-clad gap and yield strength of the clad.

4.9.2 Hot conditioning of the P.H.T. system of RAPP II (N.S.D. Elayathu)

The section has actively collaborated with the PREWAC group in the hot-conditioning of the primary heat transport (PHT) system of RAPP II. The main objective of hot conditioning is to obtain a uniform and adherent coating of magnetite which will serve as a protective layer for the carbon steel pipe lines of the system. This protective layer, besides minimising corrosion of the structural material acts as a check on the crud inventory thus controlling activity transport during operation of the reactor. The hot conditioning was conducted for 20 days during April 1977 at a temperature of about 200°C and a pressure of 80-86 Kg/cm^2 with recirculating demineralised water of pH 10.5 (adjusted by the addition of requisite amount of LiOH) and controlled low level of oxygen (less than 10 ppb) using calculated additions of hydrazine. Coupons of the various structural materials comprising the PHT system, viz. carbon steel, 304 S.S; 403 S.S; Monel-400 and Zircaloys (2 and 4) were introduced in the autoclaves installed for the purpose in a bypass to the main PHT system. The results have shown that the build up of magnetite coating on the carbon steel surfaces is fast in the initial stages, slowly reaching a plateau of thickness of 17 mg/dm^2, equivalent to 4.5 microns, at the end of hot conditioning. The adherent nature of magnetite coating was reflected in the very low crud values in the system water. X-ray analysis has established the integrity of the magnetite coating at the end of hot conditioning.

The rest of the structural materials were found to be not affected appreciably.

4.9.3 Corrosion studies in desalination systems at DEED
(P.R. Shibad and K.N. Adhe)

The committee for corrosion studies in desalination system is set up by DEED, Metallury Division and Atomic Fuels Division. The desalination group facility at DEED is being exploited for studying the corrosion behaviour of metals of interest under various conditions of desalination. The group has facilities for installing tubular samples in which the treated sea water flows inside. The tube are heated by steam from outside. Preliminary trials have been carried out so far.

4.9.4 Corrosion testing of monel tubes in alkaline solutions
(H.S. Gadiyar)

In response to a request from Atomic Fuels Division, two monel tubes with longitudinal scratches on the surface were corrosion tested in 50% NaOH at 300°C (saturation pressure) in order to check the acceptibility of these tubes with scratches for boiler application. A 15 day test has shown corrosion rate of 0.17 mils/year. There was no preferential corrosion on scratches or any cracking.

4.9.5 Plating of tin on niobium.
(A.K. Grover)

Niobium-tin (Nb_3 Sn) compound is a useful super-conducting material. To help develop the necessary technique for preparing this compound for Physical Metallurgy Section, tin plating on niobium was done from acid tin fluoborate bath. 20 to 30 micron thick tin coating was obtained at room temperature. The tin plate was given a flesh coating of opper from alkaline copper tartarate bath followed by thickness build up from acid copper sulphate bath.

4.9.6 Study of Antimony deposition
(M. Totlani and S.N. Athavale)

In response to a request from Electronics Division, study of

electroplating of antimony from fluoride bath was taken up. The bath contained antimony oxide dissolved in 40% HF. Tetrahydrofuron was added to this solution. Smooth deposite were obtained at a current density of 25 m.a/cm^2. Few electrodeposits of antimony have been supplied to Electronics Division.

4.9.7 Chromium plating of copper foils for Mossbauer studies (A.K. Grover and John T. John)

In response to a request from Isotope Division, a number of copper foils were chromium plated to a thickness of 15 to 30 microns for preparation of sources for Mossbauer studies. The copper foils were supplied by the Isotope Division. Few samples of chromium plated foils have been supplied to them.

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5. CERAMICS

The Ceramics Section is engaged in the Research and Development programmes on (1) Nuclear Ceramic materials as UO_2, UO_2-ZrO_2 and BeO, (2) Special high temperature oxide ceramics for MHD application as Al_2O_3, MgO, and rare-earth oxide stabilized ZrO_2, (3) refractory ceramics as mullite, zirconia, zircon and beryllia, (4) electrical ceramic materials as barium titanate, Ni-Zn-Ferrites, high alumina and beryllia components and high alumina substrates, (5) ceramic solid electrolytes as calcia stabilised zirconia and ThO_2-Y_2O_3 and (6) fabrication of calcium fluoride crucibles, oxide refractory ware and insulator components against specific requirements.

5.1. NUCLEAR CERAMICS

5.1.1. Development of UO_2 plate-type fuels

(S.V.K. Rao, B.D. Zope, N.S. Anandan and P.V. George)

For the Plutonium Recycle Project, the development work for the fabrication of thin sintered UO_2 platelets for making plate-type fuel elements was continued.

5.1.2. Sintering Studies on ZrO_2-UO_2

(P. Das)

Solutionising and sintering studies were continued on mixtures of UO_2-ZrO_2 containing 5 to 25 wt% UO_2 at calcination temperatures ranging from 1000°C to 1500°C, and sintering temperatures ranging from 1300° to 1560 °C. It is observed that in general, as the solutionising temperature is increased, the sinterability becomes poorer, and the maximum sinterability has been exhibited by powders solutionised at 1200°C. For the powders solutionised at temperatures upto 1200°C, it is observed that the sintered density is high increasing with increasing amount of UO_2 content and temperature of sintering. On the other hand, for powders solutionised at temperatures beyond 1200°C, the sintered density decreases as the UO_2 content is increased; also, the extent of densification decreases with increase in solutionising temperature for any given composition. Further studies are in progress.

X-ray studies indicated no unreacted UO_2 in powders solutionised

above 1200 °C. The amount of tetragonal phase formed and retained was higher with increasing temperature and additions following the phase diagram. For example, a volume percentage increase of the tetragonal phase from 8.29% to 66.05% was observed with 25% additions for powders solutionised at 1300 °C to 1560 °C as against 5.25% to 7.35% for 10% additions.

Based on the results some sintering trials at 1800 °C were taken in argon atmosphere. A very high densification for the raw materials mixed as such was observed but the high temperature tetragonal modification could not be retained completely in these samples. Powders solutionised at 1300 °C and 1500 °C, however, had shown a single phase structure (tetragonal) depending on amount of addition. For powders solutionised at 1500 °C, 20 & 25% additions had shown a completely single phase (tetragonal) in powder diffraction pattern. But for addition less than 20%, the specimens were found to be a mixture of monoclinic and tetragonal.

5.1.3. Studies on BeO.

(R. Bhat)

Investigations were carried out to study the influence of additives and calcination temperature on the powder properties and sintering behaviour of BeO derived from beryllium hydroxide.

The influence of three sintering aids viz. 1wt% MgO, TiO_2 and Fe_2O_3 on the properties of BeO powders derived by calcination of the coprecipitated hydroxide at 900°, 1000° and 1100 °C were studied. The different powder properties studied were surface area by BET method, crystallite size by x-ray line broadening and particle morphology by electron microscopy. The sintering behaviour of these powders was studied in vacuum, and the distribution of the addition by scanning electron microscopy.

The crystallite sizes calculated from three reflections (100), (002) and (102) were found to vary; the amount of variation depending on the addition. The powders calcined at 900 °C with additions had larger crystallite size (245 Å for pure and 350 Å with additive). With

increase in calcination temperature to 1100 °C, the crystallite size of the powder with MgO increased to 800 Å, whereas those with the rest of the additions increased to 550 Å. Pure BeO and BeO with MgO had a surface area of 58 and 54 m^2/gm respectively at 900 °C which decreased steeply to 3.1 & 3.5 m^2/gm at 1100 °C. In case of the powders with TiO_2 and Fe_2O_3 the fall in surface area was gradual, decreasing from 47 and 38 m^2/gm to 14.5 and 14.5 m^2/gm respectively.

The ratio of particle size to crystallite size showed large increase with increase in temperature from 900° to 1100 °C for pure powder and for the powder with MgO (increased from 1.4 and 1.1 at 900 °C to 11.5 and 7.5 at 1100 °C). The ratio increased only by a factor of 2 for the other two powders. This shows that at lower calcination temperatures, the particles consist essentially of individual crystallites. At higher calcination temperatures, the particles grow at a faster rate than the crystallites and this growth is more in case of pure BeO and in BeO with MgO. Such particle growth is retarded in case of BeO with TiO_2 and Fe_2O_3. Higher hydration tendency of the former two powders is believed to be a major factor influencing particle growth.

A common feature observed in electron microscopic study of the above powders was the presence of spherical and needle type particles along with irregular shaped particles. The majority of the fine particles were spherical especially at lower calcination temperatures. Particles with straight edges and rounded corners, plate like particles and few sintered aggregates were present in higher temperature calcined powders. The amount of needles present was more in pure BeO and in BeO with TiO_2 and scarce in the other two powders.

In case of 900 °C calcined powders when sintered in vacuum, the samples with MgO and TiO_2 attained a density of 2.7 gm/cc at 1200 °C and those with Fe_2O_3 attained 2.86 gm/cc. With increase in calcination temperature to 1000 °C, the sintered density improved to 2.84 gm/cc at 1200 °C for the samples with TiO_2 and Fe_2O_3 but reduced to 2.29 gm/cc with MgO. Higher calcination temperature of 1100 °C reduced the sintered density of the samples, especially affecting the powder with MgO which attained only 1.92 gm/cc at 1200 °C. At 1400 °C, the three samples with MgO, TiO_2 and Fe_2O_3 attained densities of 2.73, 2.9 and 2.9 gm/cc respectively. All the above additives

are found to be good sintering aids when calcined at optimum calcination temperature. The deleterious effect at higher calcination temperature especially with MgO as additive is attributed to growth of large particle and crystallites and drop in surface area.

Study of the polished and etched sintered pellets with the additives by scanning electron microscope showed a uniform distribution of the additive when the amount added is small. A higher quantity of addition of the additives was found to result in their seggregation at grain boundaries or inside the grains restricting the grain growth in case of MgO and TiO_2 additions. However, in case of Fe_2O_3 addition the grain size is enhanced and it is attributed to the formation of liquid FeO in the grain boundaries.

5.2 SPECIAL CERAMICS FOR MHD APPLICATIONS

(S.V.K. Rao, S.K. Roy, C.M. Pathak, G.T. Kamath)

The Ceramics Section has taken up the assignment of developing insulating materials and ceramic-electrode materials for the high temperature MHD channels for power generation.

5.2.1 Development of Sintered MgO

For the development of sintered MgO of optimum microstructure for MHD channel lining, a study on the alkali seed attack on magnesia was taken up on MgO bodies developed. The alkali is introduced into the plasma to increase its electrical conductivity at the operating temperature. And the successful performance of the refractories in the MHD duct depends much on the ability of material to withstand erosion by high velocity gases and corrosion by the alkali seed.

The static corrosion of magnesia by K_2CO_3 was studied. The extent of alkali attack on magnesia was evaluated by following the alkali absorption and dimensional changes of the impregnated specimens after thermal treatments, at 1300°C to 1500°C with a soaking of two hours at each of these temperatures. Microstructural changes were noted using the organic replica method.

The material formed out of an equivolume mixture of active and fused magnesia by sintering at 1500°C to a density of 85% T.D. underwent

degradation and failure at 1500°C. The weakening of the intergranular bond was evident even at 1400°C. In some of the pellets, extensive fissuring occurred. In the preliminary investigation, it was observed that incorporation of TiO_2 to the extent 5% by wt to fused magnesia aided in sintering (bulk density at 1500°C was 93% theoretical) as well as enhanced its capacity to withstand alkali attack. This aspect will be studied in detail.

5.2.2. Studies on Activated Sintering of Magnesia.

The studies on the activation of the sintering process in fused magnesia were pursued in the following categories, viz., (1) Addition of various ammonium salts NH_4F, NH_4Cl, NH_4NO_3 - in amounts upto 10% by wt. (2) Addition of decomposable salts of magnesium, viz. $MgCO_3$, $Mg(OH)_2$, $Mg(CH_3CO_2)_2$ - to the extent of 10, 25 and 50%. (3) Adsorption of inorganic acids like HF, HCl, HNO_3, H_2SO_4 and H_3PO_4 on the particle surfaces of magnesia.

In all these cases, the bulk density value on sintering reached 85% T.D.

To bring about the bulk activation in fused magnesia, minor additions of various atomic species were tried. The selection of the additives was guided by ionic size, compatibility, ability to form defect structure and ability to form liquid phase. The following oxides were added : Nb_2O_5, V_2O_5, MoO_3, Fe_2O_3, MnO_2, SiO_2, Cr_2O_3, SeO_2, TeO_2, TiO_2, NiO, B_2O_3, Cr_2O_3, CoO, Cu_2O, GeO_2, Bi_2O_3, Sb_2O_3, WO_3 and Ta_2O_5. In the preliminary studies, TiO_2, Ga_2O_3, Nb_2O_5, V_2O_5, Fe_2O_3 and NiO were found to promote densification in fused magnesia to 85%. TiO_2 addition helped sintering of fused MgO to more than 93% at 1500°C.

5.3. REFRACTORY MATERIALS

5.3.1. Studies on Stabilization of Zirconia

(P.Y. Dalvi)

During the period efforts were made to increase the densification of stabilized zirconia. The influence of thermal cycling on sintering behaviour of partially stabilized zirconia was studied.

Compacts of uncalcined mixture of zirconia containing 0.5, 2.0 & 5.1 wt% CaO were subjected to thermal cycling in two temperature ranges. i) lower range between 700-1200 °C and higher range between 700-1400 °C.

Though on 1st cycle, the sintered density decreased compared to that of those normally sintered at 1200 °C or 1400 °C with 2 hrs soaking, a steady increase in density occured as the number of cycles progressed. There was optimum density from 11 to 25 cycles (5.6 gm/cc). It was observed that the densification obtained after 25 cycles in case of higher temperature range cycling with 0.5% addition of CaO was equivalent to that obtainable by normal sintering at 1600 °C 2 hrs.

The results indicate that thermal cycling promotes densification in case of partially stabilized material compared to fully stabilised ZrO_2. This seems to be due to number of rapid phase transformations in partially stabilized ZrO_2.

5.3.2 Development of Zircon Refractories.

(A.K. Kulkarni and P.Y. Dalvi)

Thermal shock resistance tests were carried out on briquette samples made from two selected compositions using sintered zircon grog from earlier work. These briquettes were prepared from grog of graded grain sizes, and sintered at 1550°-1600 °C/2 hrs. Sintered density of the grog was within the range 3.73 and 3.77 gm/cc. The test samples were sintered at 1400 °C/2hrs and had attained density of 2.7 - 2.8 gm/cc and open porosity around 36 to 38%. These samples showed no cracks upto 20 cycles from 1400 °C to room temperature after which the test was discontinued. There was no change in densification after the test, while those sintered at 1550 °C/2 hrs and subjected to this test stood the thermal shock upto 20 cycles but some lowering in density was observed after the test was over. Ability to withstand such severe thermal shocks indicates that these samples will have good thermal shock resistance.

5.3.3. Studies on Mullitisation

(B.R. Vyas)

Studies were continued on the factors that influence mullitisation of mullite bodies. Microstructural studies on mullite bodies sintered at

1600°C for one hour were carried out using the scanning electron microscope. The following observations were made from the fractographs studied:

(i) The mullite bodies, without the incorporation of minor additions did not show any significant formation of mullite needles.

(ii) 1 wt% of minor additions of Fe_2O_3, MnO_2 or ZnO caused the formation of smaller mullite needles compared to 3 wt% additions.

(iii) The prominent interlocked mullite needles were observed in case of 3 wt% addition of equal parts of Fe_2O_3, and MnO_2; also in case of 0.2 wt% MgO and 2.5 wt% Fe_2O_3. Further microstructural work is under progress.

X-ray analysis was also carried out to compare the mullite content in the various sintered mullite bodies as listed earlier, using x-ray diffractometer and Cu $K\alpha$ radiation. X-ray diffractometer charts were taken on all the samples using Geiger Muller counter at a constant rate meter adjustment and the peaks were recorded between 15° to 70° of Bragg angles in 2 θ. The comparison of peak height for Mullite content was carried out for the strongest Bragg reflection obtained at $2\theta=26.06°$ corresponding to d=3.42 Å. The results of the data are as follows.

1) Clay as such sintered at 1400° for 2 hours gives a peak which corresponds to formation of mullite.

2) at 1600°C, the peak height ranges between (60-93%) in all the compositions of Mullite bodies.

3) 1 wt% and 3 wt% of additions of equal parts of Fe_2O_3 and MnO_2 or MgO and Fe_2O_3 enhance the peak height (72-87%) compared to 1wt% and 3 wt% additions of Fe_2O_3, MnO_2 or ZnO (57-75%).

4) Without any minor addition of mineralisers, non-calcined clay and alumina mixtures of mullite bodies give maximum peak height (93%).

Further work is in progress to study the effect of minor additions on Mullite bodies synthetically prepared from the mixture of Al_2O_3 and SiO_2 of chemically pure grade.

5.4 ELECTRICAL CERAMIC MATERIALS

5.4.1 Development of High-Alumina Components for BEL

BEL imports a large variety of high alumina components for their use. Out of these, two components of 92% alumina re required in quantities much larger than the rest. BEL requested for developing these two components in the first instance. In addition to the complexity of their shapes, they should meet the following specifications on electrical properties.

Dielectric constant (1 Mhz)	8.5
Dissipation factor (1 MHz)	0.0006
Volume resistivity at 300 °C.	10^{11} ohm-cms

This development work was taken up and 92% and 95% alumina bodies which sinter to imperviousness at 1400 °C have been developed.

When the first set of specimens of 92% alumina were fabricated and sent to BEL for evaluation, it was reported that though the specimens were completely impervious, their volume resistivity was low being 10^{11} ohm-cm at room temperature and the dissipation factor quite high being 0.0283. Based on the above results, the alumina powders were given certain leaching treatments and specimens from these were found to show a significant improvement in their electrical properties.

This work was carried out further with certain modifications and the latest set of impervious specimens prepared and sent were evaluated and it is reported that their electrical properties are very satisfactory and are in the acceptable range. The values attained are given below:

Dielectric constant	9.66
Dissipation Factor (at 1 MHz)	0.00034
Electrical Resistivity (at room temperature)	8.2×10^{14} ohm-cm

A larger number of specimens are being prepared now to establish the reproducibility of the electrical properties.

Simultaneously, the fabrication of the two dies to make the two components has been taken up with the central workshop, and trial pressings will be started on receiving the dies.

5.4.2 Development of Sintered BeO Components for BEL

(R. Bhat)

Sintered BeO discs and rings of various diameters from 5 mm to 13 mm are required for electronic application as heat sinks and washers. The requirements of such shapes are high density and zero open porosity. Preliminary studies on the fabrication of such discs were carried out with various imported BeO powders and those derived from sulphate obtained by processing one of the imported powders. Since it is difficult to sinter pure BeO to high density in air, efforts were made towards developing a suitable additive for promoting densification. Among the number of additives tried, CaO and MgO appeared effective in aiding densification. Based on these trials, numerous sintered specimens of BeO were fabricated and sent to BEL and their electrical properties have been evaluated. In some of the specimens, 1 wt% of minor additions of MgO, CaO or Fe_2O_3 had been incorporated to improve sinterability. Some of the specimens were also made from a more active BeO powder prepared by dissolving the as-received material and crystallising out as sulphate, calcining back to BeO, and then incorporating the above additions. It is observed that the dissipation factor values of all the above samples ranged from 0.00067 to 0.025 as against the specified value of 0.0002. The resistivity values ranged from 1.73×10^{10} to 1.21×10^{14} as against a stipulated value of 10^{14} ohm-cm. It is considered that a further purification of the starting BeO material, is necessary. One experimental lot of purified BeO has been prepared by the Beryllium Project. Sintered specimens are being made with this, for evaluation of the sintering behaviour and electrical properties.

5.4.3 Development of High Alumina Substrates.

(A.K. Kulkarni and D.D. Upadhyaya)

Studies on the development of high alumina substrates were

continued. During the period, techniques for minimising warpage in thin alumina substrates were established, and further trials for obtaining desired as-fired surface finish as well as grain size were made through various sintering treatments. In continuation of studies for use of antishrinkage agents, the use of pyrophyllite was studied in detail. Pyrophyllite an alumino silicate mineral, being soft and having less shrinkage and having chemical composition similar to clay was found to be a good replacement for clay, the other minor additions remaining the same as in the originally standardized high alumina body. Overall shrinkage decreased to 8% with slightly lesser density i.e., 3.4. instead of 3.6 - 3.7 gm/cc. However, the composition became impervious at 1400°C with a longer soaking period of 8 hrs. The dielectric properties were found to be identical with the earlier clay alumina bodies (K = 8-9 & D$<$.002 at 1 MHz)

Though by using pyrophyllite in place of clay and by controlling the rate of rise of temperature the warpage was reduced, to meet the specifications on flatness, use of lapping and polishing operations became necessary. However, in these operations it was observed that the surface gets contaminated with unwanted impurities and gets torn. Hence, attempts were made to obtain the required surface characteristics by controlling the surface microstructure. Desired surface finish in the as-fired state was attempted by a sintering treatment where a sintering was done at a higher temperature (1500°C) to develop the grain size to 2-3 μ. With further soaking exaggerated and non uniform grain growth takes place. So to stabilize the structure and grain size already obtained, further soak was given at a lower temperature (1400°C/7 hrs). This technique was found to be very useful to obtain uniform grain size and even grain growth.

The trials showed that with a specific sintering treatment (1500°/2 hrs + 1400°/7 hrs) desired as-fired surface finish having grain size 2-3 μ and CLA between 30-50 μ-inch could be obtained with combination of raw materials like alumina and pyrophyllite with minor additions like $MgCO_3$ & TiO_2. Samples have been submitted for further evaluation to the Electronics Division.

5.4.4 Development of High-Permittivity $BaTiO_3$ Capacitor bodies. (Ram Prasad)

(1) High Permittivity Barium Titanate Capacitors.

Barium titanate bodies with 0.1 wt% and 1 wt% additions of Ta_2O_5, Nb_2O_5, La_2O_3 and CeO_2 were prepared. These oxides were added to barium titanyl oxalate powder, which was calcined at 800°C for 4 hrs. Samples were sintered at 1250°, 1300° and 1400°C for 2 hrs in air. The effect of other sintering atmospheres like vacuum, nitrogen and hydrogen was also studied. Samples sintered in hydrogen atmosphere were sintered in air at temperatures of 800°C, 1000° and 1200°C for 2 hrs. Some samples were given an extended soaking of 16 hrs also. The physical and dielectric properties of sintered samples were determined.

It was observed that the sintering treatment and the nature and concentration of the additives have a pronounced influence on the dielectric properties of barium titanate. In pure $BaTiO_3$ powders or with higher concentration of additives, high dielectric constants ($\sim$ 40,000-50,000) were obtained by first reducing the material in hydrogen and then reoxidising in air at $\sim$ 1000°C. In comparison to this, for powders with small concentration of additives, high dielectric constants ($\sim$ 100,000) could be obtained in a single sintering treatment in air. Sintering in nitrogen or vacuum yielded even higher K values. These were of the order of 177,000 (La_2O_3, N_2) 170,000 CeO_2, (vacuum), 158,000 (Nb_2O_5, N_2) and 101,000 (Ta_2O_5, N_2). Higher sintering temperature, longer soaking period or a higher concentration of additives resulted in much lower values of dielectric constant. Hence, it was possible to obtain barium titanate ceramics with very high dielectric constant and reasonably low dissipation factor by a suitable choice of the additives, the sintering temperature and the furnace atmosphere.

5.4.5 Development of Ni-Zn-Ferrites

(Ram Prasad)

Magnetic Fluids:

Development of suitable magentic fluid for application in high-

vacuum magnetic seals, as required by Nuclear Physics Division was continued. Efforts were made to form stable suspensions of Ni-Zn-Ferrite powders in high-vacuum oil. The powders were obtained by three different routes, viz. calcination of co-precipitated oxalates, direct precipitation of ferrite in highly alkaline medium and solid state reaction of the component oxides. Formation of a stable suspension was facilitated by grinding in an agate planetary mill and using oleic acid as dispersing agent. Amongst the various concentrations of oleic acid used, a 10 vol% of oleic acid in vacuum oil was the most successful. It was observed as a result of extensive laboratory trials that ferrite powders, obtained from oxalate route or solid state reaction, when suspended in vacuum oil containing 10 vol% oleic acid yielded stable suspensions after 150 hrs of milling. Further work is in progress.

5.5 DEVELOPMENT OF CERAMIC SOLID ELECTROLYTES

(S. Ramanathan and S.K. Roy)

The development of YDT (Yttria doped thoria) electrolytes was pursued. Compacts of YDT material prepared by the Sol Gel method in the form of spheres having a diameter of 400 microns were sintered in flowing H_2 atmosphere. The sintering behaviour was found to be very poor.

To produce sinterable YDT powder, calcination of coprecipitated oxalates of Th^{4+} and Y^{3+} and also of mixed nitrates was carried out. The calcination was carried out at 900°C/6hrs. in air. The samples were isostatically pressed at 20,000 psi and sintered at 1500°C/5 hrs. The oxalate-derived samples sintered to about 86% T.D. The nitrate-calcined powder yielded samples with 76% density.

The solid solution formation during calcination was followed by X-ray diffraction method. While the nitrates yielded solid-solution of Y^{3+} in ThO_2 readily on calcination, the oxalate resulted in mixed oxides only. Sintering of YDT samples at higher temperatures to attain better density is being attempted.

5.6 DEVELOPMENT OF CERMETS

(P.K. Agnihotri)

Development of various Composites/Cermets received much attention in the search of high temperature materials for various applications requiring adequate strength and hardness which in turn depend on the particle size of the dispersed hard phase in a given composition.

Composites are defined as two or more dissimilar materials intimately bonded to form an integral structure to attain improved properties. Structural cermets are particulate composites of Metal/Cermics. Bonding of heterogenous phases takes place by mass transport in solid state, whereas in liquid phase sintering action of chemical potential gradients and surface tension forces are important.

An assignment hasbeen taken up to develop Nickel Alumina composites. In this work, major effort was made to develop particulate composites of Ni/Al_2O_3 by Nickel coating of Alumina particles through mechanical alloying. For this purpose a mixture of fine alumina powder 0.06 micron size and freeze-dried Nickel powder of 500 Å particle size was used. Metal coated alumina powder particles were obtainedby micronising the powder mixtures. The Nickel contents chosen in these cermets were 10% 20% and 30% by wt.

Cold pressed samples from these coated powders were sintered at 1200°C and 1500°C respectively for one hour. Specimens sintered at 1200°C were found to be porous having poor strength. However, samples sintered at 1500°C had good densification of the order of 89% theoretical and good strength. Further densification of the order of 95% theoretical could be obtained by prolonged soaking for 8-10 hrs at 1500°C.

5.7 STUDIES ON SINTERING MECHANISM

5.7.1 Studies on Oxide Powders

(G. Eswara Prasad)

It has been established that the origin and the thermal

history of oxide powders have a major influence on their crystallinity which in turn affects their sintering behaviour. It is hence felt that the material movement during sintering depends strongly on the degree of crystallinity of an oxide powder. A study was made to examine the behaviour of powders having different degrees of crystallinity and to assess crystallinity quantitatively.

In-situ electron beam heating studies in the transmission electron microscope on different materials (amorphous and crystalline) were conducted with a view to following the sintering process. These studies showed significant morphological changes in the powders during sintering. Subsequently, some selected samples were studied in the hot stage of the electron microscope at temperatures upto 1040°C, using a constant low beam current to observe the difference in the sintering behaviour of different powders. An attempt was also made to study the thermal decomposition - induced evolution of magnesia from magnesium hydroxide. For these studies, a technique was developed in which a thin film of magnesium hydroxide was prepared on nickel grid. Hot stage microscopy was carried out on this film to follow the development of crystallinity in the magnesia powders derived from three parent compounds - hydroxide, carbonate and oxalate - at various calcination temperatures ranging between 400° - 1200°C and Warren and Averbach's method was used to evaluate strain and effective domain size. The percentage degree of crystallinity was calculated using crystallinity index method of Wakelin, Virgin and Crystal. Microstructural changes that took place in sintered magnesia pellets were studied under the scanning electron microscope. These pellets were prepared from magnesia obtained from magnesium hydroxide and the magnesium oxalate on calcination at 800°C and also from fused magnesia and the temperatures used for sintering ranged from 900°C to 1400°C in air for two hours under identical conditions.

The following conclusions could be arrived at on the basis of the observations made in the above work:

1) Oxide powders derived from different parent compounds by calcination do not have residual microstrains as revealed by x-ray line profile analysis.

2) The degree of crystallinity is a more important parameter than the crystallite size in relation to the sinterability of an oxide powder.

3) The origin of an oxide powder has a significant influence on the process occuring during calcination, hence on the degree of crystallinity, the crystallite size and the particle size of the powder.

4) Sinterability and microstructural development can be correlated with the rates of change of the degree of crystallinity, the crystallite size and the particle size with temperature.

5) Nucleation and grain growth can be noticed only after the degree of crystallinity attains a certain minimum value, generally over 75%.

6) When a powder is poorly crystalline, the mechanism of densification is akin to that in an amorphous powder like glass.

The sinterability and the progress of densification depend on the rate of change of crystallinity, particle size, crystallite size and the development of microstructure.

5.7.2 Studies on Sintering Diagrams.

(Ashok Mohan and N.C. Soni)

The mechanisms by which material movement takes place during sintering are not only interesting but also very important in determining the properties of the end product and suitable sintering schedules etc. In spite of substantial efforts invested in this field, the agreement on issuesis only limited. The classical exponent method, initially proposed by Kuczynski, has resolved the issue to an extent and has been the mainstay of this field. However, it has handicaps which could not be by-passed. Ashby has recently broken away from the classical approach and has suggested a method of constructing what he calls the sintering diagrams. The area defined

by axes representing normalised neck size (x/a) and homologous temperatures (T/T_m) is divided into fields in which a mechanism is predominant. This is determined with the help of suitable rate equations representing the mechanism. The other variables that he has contented with are particle size (a) and initial pore volume fraction (f). This method resolves major problems in the exponent method like ambiguity in criterion and a simultaneous consideration of a large number of mechanisms and sintering variables becomes possible.

Although Ashby's method has great potentialities, the exercise gets increasingly complicated as the number of mechanisms and/or variables are increased. To overcome this, a computer programme has been designed in this effort. In addition, a new method of constructing sintering diagrams is suggested. The computer output is in the form of *Relative Contribution Diagrams (RCD)*. Each situation defined by x/a and $\frac{T}{T_m}$ is represented by a space in which a group of 25 digits are printed. The number of times that a digit is repeated gives the contribution of the mechanism that it represents.

The additional advantages gained by this new method of construction are (a) The extent of predominance is revealed (b) It is possible to predict circumstances under which the contribution of a mechanism would change (c) The speed with which a mechanism gives way to another with change in one parameter is clearly seen. This could be very useful in establishing sintering schedules.

Work is being extended with the help of RCD and a rationalised basis has been suggested for determining x/a at which the stages of sintering change. The diagrams are also being used to study sintering mechanisms in UO_2. This study is revealing important sintering variables and properties of the material that influence the relative contribution of mechanisms.

5.8 ADVANCED HIGH TEMPERATURE AND MATERIALS DEVELOPMENT PROGRAMME
(Co-ordinator: Ashok Mohan)

A need for a facility to generate high temperatures has been realised. Especially for development of materials capable of

surviving severe conditions that are, at times, encountered in nuclear and space industries. A group has been formed to look into the alternatives for high temperature generation. A preliminary report is to be prepared f~ identifying potential methods of generation, direction in which the initial research efforts need to be made and to broadly determine the nature and quantum of inputs required.

The first leg of the programme consists of developing systems like plasma heating and ion bombardment, which are parts of ongoing programmes. Second leg consists of extending the present systems to higher levels of temperatures. The initial efforts regarding the latter have been started by way of modifying the existing design of Molybdenum resistance furnace to obtain substantially higher temperatures than the present level of about 1800 °C. Possibilities of using lasers to advantage in high temperature generation and materials research have also been investigated.

5.9 STATUS REPORT ON FUSION TECHNOLOGY

(Ashok Mohan)

A report on the status of Fusion Technology has been prepared. For this, the alternative approaches of current interest both in magnetic and inertial confinement, have been studied. A perspective on the plans in the light of the targets and magnitude of investments has been developed. The problems being faced were identified as also the gap between available and required technology. Information on related subjects like environmental impact of fusion devices, authoritative opinions on current status, materials requirements in fusion systems etc. has also been appended to the report that has been prepared.

5.10 CERAMICS FABRICATIONS

(S.V.K. Rao and B.D. Zope)

In the Ceramic fabrication facilities of the Section, from time to time various items of ceramic products were fabricated and supplied to diverse users under DAE. Some of such items supplied are give below.

(1) Alumina shapes 5.6 ± 0.05 mm in diameter with four holes for NPD (225 Nos.)

(2) Thermal shock resistant alumina body from fused grains of alumina suitable for the fabrication of NFC trays.

(3) Ceramic nozzles for sand blasting

(4) Button shaped ceramic pieces ,3000 Nos. and a suitable raw glaze for the above pieces for the Isotope Division

(5) Alumina rods 3 mm dia and 250 mm length for the flame spraying gun for RED.

(6) Crystal seed holders for TPD

(7) CaF_2 crucibles for Radio Chemistry Division

LIST OF PAPERS PUBLISHED/ACCEPTED/COMMUNICATED FOR PUBLICATION/PRESENTED DURING THE YEAR 1977

1. Gas distributors in fluidied beds:
D. Sathiyamoorty & Ch. Sridhra Rao
Accepted for publication in Powder Technology, U.K.

2. Bubbles at the Gas Distributors in Fluidied Beds
D. Sathiyamoorty & Ch. Sidhra Rao
Presented at the 7th National Conference on Fluid Mechanics and Fluid Power (Nov. 1977)

3. Multi orifice Plate Distributors in Gas Fluidiser Beds - A Model for the Design of Gas Distributors.
D. Sathiyamoorthy & Ch. Sridhsra Rao
Communicated for publication in Powder Technology

4. Studies on Electrorefining of Calciothermic Hafnium
I.G. Sharma and C.K. Gupta
J. of Nuclear Materials, 74(1978) 19-26.

5. Pilot-plant Production of Niobium.
C. Narayanan, T.K. Mukherjee, D.K. Bose & C.K. Gupta
Trans. I.I.M. 30 (Dec. 1977) 387-94

6. An Evaluation of Vanadium Oxycarbide as Ladle Addition of Molten Steels
D.K. Bose & C.K. Gupta
Met. Trans B, 8B (Dec. 1977) 601

7. Pyro and Hydro-metallurgy of Nickel and Molybdenum Extraction from their Sulphides
A.K. Suri, T.K. Mukherjee, D.K. Bose & C.K. Gupta
Presented at the International Conference on Metal Science - The Emerging Frontiers
Varanasi Nov. 23-24, 1977

8. The Development of a flow-sheet for processing Indian Nickel-Copper Sulphide Concentrates.
P.P. Shukla, T.K. Mukherjee and C.K. Gupta, Met. Division
R.A. Nagle, K.S. Koppikar & T.K.S. Murthy, Chemical Engg. Divn.
Accepted for Publication in Trans. Inst. of Mining & Met. (Sec C).

9. Electrometallurgical research at the Extractive Metallurgy Section, Bhabha Atomic Research Centre.
T.K. Mukherjee & C.K. Gupta.
Surface Technology, Vol.7, No.5 (1978) 347-352

10. A Chloridising Roasting route to Recover Nickel from a Sulphide Concentrate
P.P. Shukla, T.K. Mukherjee, C.K. Gupta
Presented at the 31st Annual Tech. Meeting of I.I.M. held at I.I.T. Madras, 14-16 Nov. 1977

11. Production of Chromium by Molten Salt Electrolysis
A.K. Suri & C.K. Gupta
Surface Technology 5 (1977) 271-276

12. Studies on the fabrication of aluminium bonded boron carbide rings
A.K. Suri & C.K. Gupta
Accepted for publication in J. of Nuclear Materials

13. Development of graphite lubricated fuel for heavy water power reactors.
T.K. Mukherjee & C.K. Gupta
Technical Report, BARC

14. On the aluminothermic reduction of calcium vanadate.
O.K. Mehra & C.K. Gupta
Met. Trans B, 8B (Dec. 1977) 683

15. Some aspects of pilot plant production of Micron size Zirconium Powder by Calciothermic Reduction of Zirconium Oxide.
S. Chaudhary & T.S. Krishnan
Trans. IIM 30-4 (1977)224

16. Decomposition of Zircon by Soda Ash Sintering Process.
P.R. Menon, J.M. Juneja & T.S. Krishnan
Accepted for publication in Trans. Inst. of Mining and Metallurgy, U.K.

17. Application of free energy - composition diagrams in predicting the sequences of phase transformations in Zirconium - Niobium alloys.
E.S.K. Menon, S. Banerjee & R. Krishnan
To be published in Metallurgical Transactions

18. Kinetics of alpha precipitation in Ti-6 wt% Cr and Ti - 11 wt% Mo.
M. Unnikrishnan, E.S.K. Menon & S. Banerjee
To be published in Journal of Materials Science.

19. Non-equilibrium precipitation in Zr-5 Ta.
E.S.K. Menon & P. Mukhopadhyay
To be published in International Journal of Metallography.

20. Discontinuous precipitation in a Martensite
P. Mukhopadhyay & V. Raman
To be published in International Journal of Metallography

21. Formation of a DO_{19} phase in Zirconium-Aluminium martensites.
P. Mukhopadhyay, V. Raman, S. Banerjee & R. Krishnan
To be published in Journal of Materials Science

22. The effect of heat treatment variables on the structure of commercial Ti-8Al-1Mo-1V alloy
S.J. Vijayakar, S. Banerjee & R. Krishnan
To be published in Trans. IIM.

23. Applications of transmission electron microscopy in phase transformations
S. Banerjee
Presented at the DAE Materials Science Symposium, Rourkela, October, 1977.

24. Structure property correlation in the alloy Ti-8Al-1Mo-1V
S.J. Vijayakar, S. Banerjee & R. Krishnan
ibid

25. Phase transformation in Zirconium alloys
R. Krishnan
Presented at International Conference on Metal Sciences
Varanasi
November, 1977

26 Micorduplex structure in the Ti-6Al-4V alloys.
S.J. Vijayakar, S. Banerjee & R. Krishnan
ibid

27. Phase separation in the Ti-34 at% Nb alloy.
E.S.K. Menon, S. Banerjee & R. Krishnan
ibid

28. Precipitation in dilute Zr-Sn alloys
Uma Naik & S. Banerjee
ibid

29. Influence of second phase dispersion on void formation during irradiation
M. Sunderaraman, S. Banerjee & R. Krishnan
Presented at the Indo-German Seminar on Radiation Damage, Kalpakkam
Nov. 1977

30. Blistering by ion bombardment
D.K. Sood, M. Sundararaman & R. Krishnan
Presented at Surface Science Symposium, Bombay
Feb. 1977

31. Coherency strain contrast around Ni_3Nb precipitates
M. Sundararaman & S. Banerjee
Presented at Tenth Annual Conference of Electron Microscope Society of India, Bombay
December 1977

32. Precipitation reactions in a PH 13-8Mo stainless steel
V. Seetharaman, M. Sundararaman & R. Krishnan
ibid

33. Fractographic investigations on Ti-15% Mo
Uma Naik, G.E. Prasad & S. Banerjee
ibid

34. Quenched and tempered structures in Zr-5Ta
E.S.K. Menon, P. Mukhopadhyay & S. Banerjee
ibid

35. Variations in work hardening and dislocation structures with diformation temperature in Zirconium & Titanium
P. Rodrignez, P. Mukhopadhyay, S.S. Vagarali & R. Krishnan
ibid

36. Strength and deformation behaviour of Zirconium-Titanium martensites
S. Banerjee, S.J. Vijayakar & R. Krishnan
Communicated to Acta Metallurgica

37. Incompressibility of atoms in intermetallic phases with LI_2 and DO_{19} structures: a lattice parameter approach
E.S.K. Menon & P. Mukhopadhyay
Communicated to Materials Research Bulletin

38. Strain ageing in Zirconium - 2.5 wt% niobium alloy
T.K. Sinha & M.K. Asundi
Journal of Nuclear Materials, 67 (1977) 315

39. Effect of strain rate and temperature on tensile properties of heat treated Zirconium - 2.5 wt% niobium alloy
T.K. Sinha & M.K. Asundi
Journal of Nuclear Materials, 67 (1977) 311

40. Deformation of the martensite in Zr-1.5Sn and Zircaloy-2,
V. Raman & P. Mukhopadhyay
To be published in Journal of Materials Science

41. Mechanical equation of state in Zirconium alloys
V. Raman & P. Mukhopadhyay
To be published in Physica Status Solidi

42. Internal friction measurements in a V-20Ti alloy containing Oxygen
S. Mishra & S.S. Vagarali
Presented at the DAE Materials Science Symposium, Rourkela, October, 1977

43. Strength of dilute zirconium-copper martensites
S.L. Wadekar, V. Raman & P. Mukhopadhyay
ibid

44. Mechanical equation of state in Zirconium alloys
V. Raman & P. Mukhopadhyay
Presented at the International Conference on Metals Sciences, Varanasi, November, 1977

45. Internal friction techniques in the study of radiation induced damage
S. Mishra
Presented at the Indo-German Seminar on Radiation Damage, Kalpakkam, November, 1977

46. Evaluation of materials for End- shields in CANDU reactors
V.V. Raman
ibid

47. A new method for the evaluation of internal stress for stress-strain transients
V.V. Raman & M.K. Asundi
Communicated to Acta Metallurgica

48. Mechanical Behaviour of quenched and neutron irradiated Zirconium, Zircaloy-2 and Zr-1% Al alloy
M.K. Matta, I.S. Batra & B.D. Sharma
Trans IIM 30 (1977) 240

49. Point defect Behaviour & phase stability problems in alloys
B.D. Sharma
Presented at Indo-German Seminar on Radiation Damage, Kalpakkam Nov. 1977

50. Spontaneous vacancy condensation on Gas Bubbles
G.P. Tiwari
ibid

51. Defect structure & post irradiation Annealing in neutron irradiation Nickel base alloys
I.S. Batra, M.K. Matta & B.D. Sharma
Trans. IIM 30 (1977) 92

52. X - Particle irradiation induced precipitation and phase instability in concentrated Fe-Cr-Ni alloys
B.D. Sharma et.al
To be published in Radiation Effects Journal

53. Isochronal Annealing of Electrical Resistivity of Electron irradiated concentrated Fe-Cr-Ni alloys
B.D. Sharma et.al
To be published in Phil. Mag.

54. Position Annihilation studieson Electron and X - particle irradiated 75 Ni-13Cr-12Fe alloy
S. Mantl, B.D. Sharma & G. Antesberger
Communicated to Phil. Mag.

55. A correlation between vacancy formation energy and compressibility
R.V. Patil & G.P. Tiwari
Indian J. Pure and Appl. Phys. 15-3 (1977) 206

56. Modification of Richards Rule and Correlation between entropy of Fusion and allotropic behaviour
G.P. Tiwari
To be published in Metal Science Journal

57. The correlation between the entropy of Fusion and the diffusion behaviour
G.P. Tiwari
To be published in Trans. Japan Institute of Metals

58. A phenomenological model for diffusion in solids
G.P. Tiwari
Submitted for publication in Trans. Japan Institute of Metals.

59. Chemical Diffusion studies in Titanium- Iron system
G.B. Kale, S.V. Khera & G.P. Tiwari
Presented at Annual Technical Meeting of IIM, Madras, Nov. 1977

60. Dissolution Kinetics of Zirconium Hydride
M.D. Vora, K.S. Shivaramkrishnan & G.P. Tiwari
Submitted for publication in Trans. IIM

61. Failure of Stainless steel line carrying He to CIRUS reactor vessel tube sheet
R.C. Pant & H.S. Gadiyar
Presdnted at the Symposium on operating experience of Nuclear Reactors and Power Plants; Feb 7-9, 1977, BARC

62. Aluminium base Mg alloys for Desalination
H.S. Gadiyar, N.S.D. Elayathu & V.P. Joshi
Presented at the Symposium on 'Protection of Materials in the Sea' held on 25-26 Feb, 1977 at Naval Chemical and Metallurgical Lab, Bombay

63. Corrosion of carbon steel in high temperature: dissolved oxygen and pH effects
S. Chakravarty & H.S. Gadiyar
Presented at the 1st National Conf. on 'Corrosion and its Control' RRL, Hyderabad, 26-28 June 1977

64. Ellipsometry in Surface Film Analysis
S. Chakravarty & H.S. Gadiyar
Presented at the 7th DAE Materials Science Symposium, Rourkela, Oct. 1977.

65. Effect of impurity elements Al, Mn & N_2 on the corrosion resistance of Zircaloy-2 in high temperature water and steam
H.S. Gadiyar - Presented at the International Conference on Metal Sciences - The Emerging Frontiers Nov. 23-26, 1977, Varanasi

66. Corrosion behaviour of wrought & electrodeposited nickel in alkaline environments - Effect of ammonia, sulphide & Chloride
P.K. De, S.K. Ghosal & K. Elayaperumal
ibid

67. Corrosion Studies of Cu-9%Sn-4%Al alloy for salt water service
Presented at the symposium on Protection of Materials in the Sea held at NCML Bombay during February 25-26, 1977
P.R. Shibad & K. Elayaperumal

68. Corrosion properties of nickel free austenitic stainless steel as compared to 18/8 stainless steel
P.R. Shibad
Presented at the 1st National Conference on "Corrosion and its Control." held at Hyderabad, June 26-28, 1977

69. A Recent Case study of Boiler Tube Failure
K. Elayaperumal
ibid

70. Structure Dependent Corrosion of Metals & Alloys
K. Elayaperumal
Presented at the DAE Materials Science Symposium, Rourkela, Oct. 1977

71. Some Typical Corrosion Failures in Chemical and Process Industries and their Prevention
K. Elayaperumal
Chemical Concepts Feb, 1977

72. Electroforming of Porous nickel tubes
A.K. Grover & J.T. John
Presented at the 31st Annual Tech. Meeting of Indian Institute of Metals, Madras, Nov. 1977

73. Fine tungsten metal powder by hydrogen reduction of WO_3
P.R. Singh, M. Totlani & J. Balachandra
To be published in Trans. IIM

74. Corrosion Problems in Nuclear Power Plants; Types, Analyses and Remedial Measures
K. Elayaperumal & C.V. Sundaram
Presented at the DAE Symposium on Operating Experience of Nuclear Power Reactors & Power Stations, BARC, Feb. 1977

75. Physico-chemical Studies on Powders and their sinterability Sintering of Uranium Dioxide Powders
N.C. Soni, Ph.D. Thesis (1977)

76. Studies on the Sintering of Beryllia - Influence of Minor Additions on Sintering of Beryllia Powders
R. Bhat, Ph.D. Thesis (1977)

77. Studies on the Mechanisms of Sintering - Sinterability of Oxide Powders
G. Eswara Prasad, Ph.D. Thesis, 1977

78. High Permittivity Barrier and Boundary Layer Capacitors
K. Thiagarajan, Ram Prasad & S.V.K. Rao
Presented at the Symposium on "Surface Phenomena in Metallurgical Processes", held at IIT, Bombay, 19-20 Feb, 1977

79. Ceramic Surfaces Related to the Sintering Processes
S.K. Roy, C.M. Patha & S.V.K. Rao
ibid

80. Influence of Calcia Addition and Calcination Temperature on Sintering and Stabilisation of Zirconia
P.Y. Dalvi & V.K. Moorthy
Presented at the 41st Annual Technical Meeting of the Indian Ceramic Society, Bangalore, 28-30 April 1977

81. Influence of Minor Additions and Sintering Treatments on the Density and Microstructure of Sintered Urania Pellets
N.S. Anandan & V.K. Moorthy
ibid

82. Improvement of Properties of Sinterable Uranium Dioxide Powders
N.C. Soni & V.K. Moorthy
Trans. Ind. Cer. Soc. 36-2 (1977) 26

83. Sintering Mechanism Diagrams
Ashok Mohan, N.C. Soni, V.K. Jain & V.K. Moorthy
To be published in Science of Sintering Journal.

84. High Temperature Phase Diagram for Zr-Mo and Hf-Mo
S.P. Garg and R.J. Ackermann
Met. Trans. 8A (1977), 239.

85. High Temperature Phase Diagram for Th-Mo, Th-Re, U-Mo and U-Re; Derived Thermodynamic Properties of Refractory Metal Solutes in Liquid U & Th
S.P. Garg and R.J. Ackermann
J. Nucl. Mater. 64 (1977), 265.

86. High Temperature Phase Diagram for Zr-O
R.J. Ackermann, S.P. Garg and E.G. Rauh
J. Am. Ceram. Soc. 60 (1977) 341.

87. Refining of Reactive Metals
C.V. Sundaram, S.P. Garg and J.C. Sehra
Presented at the International Conference on 'Metal Sciences - The Emerging Frontiers, BHU, Varanasi, 1977.

88. Beryllium Development Programme in India
K.S. Subbarao, B.P. Sharma, C.M. Paul and C.V. Sundaram
Presented at the International Conference on 'Beryllium', 1977 (Metals Society, London, October, 1977).

89. Special Metals Development - Assessments and Projections
C.K. Gupta and C.V. Sundaram
Presented in Conference on 'Recent Developments in Non-ferrous Metal Technology', Indian Institute of Science, Bangalore, 1977.

METALLURGY COLLOQUIM SERIES

The following list gives the lectures held under Metallurgy Colloquim during the year 1977.

Sr.No.	Date	Speaker	Topic
1	5.1.77	Dr.B.V. Narasimha Rao University of California, Berkeley	Phase Transformations and Design of Alloys
2	18.1.77	Prof. Khulman Wilsdorf Univ. of Virginia, Virginia	Bardeen-Herring Climb Versus Vacancy Precipitation at Dislocations
3	2.3.77	Dr. A.M. Gokhale IIT Kanpur	Quantitative Metallography
4	17.3.77	Dr.M. Nageswara Rao Midhani, Hyderabad	Fatigue Crack Propagation in Precipitation Hardening Aluminium Alloys
5	23.3.77	Shri A.K. Suri Metallurgy Division	Electrometallurgical Methods of molybdenum production
6	15.4.77	Dr.S. Mishra Metallurgy Division	Anelasticity in Zr,Ti and their alloys
7	7.5.77	Shri Sohan Singh Met. Divn.	Rare earth Metals extraction technology
8	31.5.77	Dr.S. Risbud Univ. of Nebraska Lincoln, USA	Subliquidus Immiscibility as an Essential Precursor to crystallization of silica-alumina metals
9	19.7.77	Shri Ch.Sridhar Rao Met. Divn.	Structure and Behaviou Fluidised beds
10	25.8.77	Dr.G. Venkataraman RRC	Stochastic approach to Anelastic creep
11	6.10.77	Shri K.S.Subba Rao Met. Divn.	Powder Metallurgy of Beryllium

1 Sr.No.	Date	Speaker	Topic
12	10.11.77	Dr.K.H. Westmacott Lawrence Berkeley Lab., USA	The effect of interstitial Impurities in Secondary Defect Formation in Quenched Metals
13	16.11.77	Prof.H.I. Aaranson Michigan Technological Univ., USA.	Solid-solid Nucleation Theory: Extensions, Testing & Applications.
14	17.11.77	Prof. Newmann Max Planck Institut at Dusseldorf	Fracture Mechanisms
15	18.11.77	Prof. M.C. Flemings MIT, USA	Recent advances in solidification technology
16	21.11.77	Dr.W. Schilling KFA, Julich	Self Interstitials in Metals
17	1.12.77	Dr.G. Ostberg AB Atomenergie, Sweden	Safety and Reliability of Nuclear Pressure Vessels and Ancillaries
18	3.12.77	Prof.J. Levy Ecole des Mines, Paris	High temperature phase transformations in stainless steels.

Extractive Metallurgy Section

Dr. C.K. Gupta, SO(SF)
(Head of Section)

NFC Projects

New units of Special Materials Plant.

Titanium Pilot Plant 7.5 t/y

Research & Development on Refractory Metals

DK Bose (SE)

- *AK Suri (SD)
- OK Mehra (SC)
- C Narayanan (SB)
- KU Nair SA(C)

Project planning for B_4C production and fabrication, Preparation of boron, boral. Metallothermy of oxides, halides & sulphides of refractory metals (Nb,Ta,V,Mo,W) and carbothermy of (Nb & Ta) for metal, ferro-alloy and super alloy preparation.

TK Mukherjee (SE)

- BR Mahendra (SD)
- Sudhir Nanda (C)
- PP Shukla (SC)
- PVS Pillai SA(C)

Developments relating to graphite coated fuel and plasma technology. Extraction of Mo and Ni from their respective sulphide intermediates and electro-extraction of refractory metals.

Process Development & Basic Research

TS Krishnan (SE)

- Smt. IS Thomas(SC)
- PR Menon SA(C)
- PK Rajagopalan SA(C)
- RP Tangri SA(B)

Development and fabrication of $R(CO)_5$ (R.E.) alloys for permanent magnets. Development of TiC for heating and routine spectrochemical analysis of refractory metals.

JC Sehra (SE)

- PL Vijay (SD)
- IG Sharma(SD)
- A Unnikrishnan SA(C)

Reclamation of Zr & Ti from scraps. Studies on magnesiothermic reduction of rutile, HfO_2. Purification of crude metal by molten salt electrorefining & iodide process. Fabrication of Hf shapes.

SP Garg (SE)

- R Venkataramani (SD)
- JM Juneja(SD)
- N Krishnamoorthy (C)
- YJ Bhatt (SC)

Thermodynamic studies of alloy systems and oxide-carbide reactions. EMF measurements of solid electrolyte system. Development of solid electrolytic galvanic cell technique for thermodynamic evaluation

Titanium Technology

Ch. Sridhar Rao (SE)

- D Sathiyamoorthy (C)
- C Subramanian (SC)
- K Swaminathan SA(C)

Basic and Applied (Roasting, Oxidation, pyro-carbon coating), Studies on fluidisation. Fused salt electrolysis of $TiCl_4$. Oxidation of industrial $FeCl_2$ solution.

<u>Admn.& Supporting Staff</u>

Stenographer (SE)

* [illegible] to USA

Beryllium Project Section

CM Paul, SE

B.P.P. Project

KS Subbarao	D
BP Sharma	SD
JS Nair	SC

Setting up of the Beryllium Pilot Plant at Vashi, New Bombay : Design of plant, equipment and machinery; Co-ordination of civil, electrical and ventilation works; Procurement, testing and erection and commissioning of equipment and machinery.

Development Programmes

SA Kulkarni	C
VD Shah	SC
MG Rajadhyaksha	SC
RH Rakhasia	SA(C)
K Mammdu	SA(C)

Studies on the preparation of beryllium metal, starting with Indian beryl and Cu-Be alloys - Fabrication of Be metal and Cu-Be alloys - ultra purification of rare metals.

<u>Supporting Staff</u>

AD Salunke T'man (C)

Physical Metallurgy Section

Dr.M.K. Asundi, SO(SF)
(Head of Section)

Metal Physics Group

Dr. B.D.Sharma	(SF)
Dr. G.P.Tiwari	(SE)
Dr. P.K.K.Nayar	(SE)
MC Saxena	(SD)
SK Khera	(SD)
GB Kale	(SD)
VV Utgi	(SC)
RV Patil	(SC)
IS Batra	(SC)
MN Vijayakumar	(SC)
KC Paliwal	SA(B)

1. Tracer diffusion studies in metals and alloys
2. Irradiation effects on mechanical properties of metals and alloys, studies on nucleation and growth of voids and bubbles.
3. Precipitation and diffusion controlled reaction in Zr-base alloys.

Adm. & Supporting Staff

Stenographer	1
Foreman	1
Draughtsman A	1
Tradesman G	1
Tradesman F	1
Tradesman E	2
Tradesman D	2
Tradesman C	4
Tradesman B	1

Structural Studies Group

Dr.R. Krishnan	(SF)
CN Rao	(SE)
Dr.S. Banerjee	(E)
P Mukhopadhyay	(SD)
SJ Vijayakar	(SD)
Lalit Kumar	(SD)
Smt. Uma Naik	(SD)
ESK Menon	(C)
UD Kulkarni	(C)
M Sundararaman	(SC)
M Unnikrishnan	(SC)
MD Vora	(SB)
EG Baburaj	SA(C)
Kum.J.J.Agarwal	SA(B)

1. Thin film transmission electron microscopy of Zr and Ti-base alloys
2. Correlation of mechanical properties with electron microstructure in Ti-6Al-4V
3. Study of hydride precipitation in zirconium and its alloys

Technical Services

RN Arya	(SE)

Supervision of Divisional Workshop, fabrication and maintenance of equipment.

Adm. & Supporting Staff (contd..)

Helper B	1

Mechanical Properties Group

P Dasgupta*	(SE)
TK Sinha	(SE)
RN Tank	(SD)
S Mishra	(SD)
VN Sathe	(SD)
V Venkitaraman	(SD)
V Raman	(C)
JK Chakravarthy	(C)
NT Parekh	SA(C)
AB Tamhane	SA(B)
SL Wadekar	SA(B)
R Kishore	SA(A)

*On deputation abroad at France.

1. Strengthening mechanisms in zirconium alloys
2. Thermally activated deformation studies
3. Internal friction studies due to solutes in HCP metals
4. Melting and fabrication of alloys particularly of alloys of nuclear industrial importance.

Corrosion and Electrometallurgy Section

Dr. K. Elayaperumal, S.O.(SF)

(Head of Section)

Corrosion

Materials for Reactor Applications

Dr HS Gadiyar	(SE)
SS Chouthai	(SE)
FK De	(SD)
SV Phadnis	(SD)
GC Palit	(SC)
SK Ghosal	(C)
KB Gaonkar	(SA-'B')

Studies on zirconium alloys, aluminium alloys, carbon steels and stainless steels.

Materials for Desalination Systems

NSD Elayathu	(SD)
PR Shibad	(SD)
KN Adhe	(SA-'B')

Studies on Al-base, Cu base and Ti-base alloys.

Basic studies on corrosion

Consultancy service and Assistance

Electrometallurgy

Hydrometallurgy and Electrowinning

M Totlani	(SE)
Sohan Singh	(SD)
PR Singh	(SC)
AL Pappachan	(SA-'C')
SN Athavale	(SA-'C')
MN Joshi	(SA-'C')

Nickel recovery from dilute solutions

Electrowinning of Rare Earth Metals.

Electrodeposition of metal/oxide composites

Electroplating and Electroforming

AK Grover	(SD)
PG Deshpande	(SD)
A Ramasamy	(SC)
JT John	(SC)

Electroplating of specific metals and alloys.

Electroforming of special metallic parts.

Electrophoretic Deposition.

Administrative & Supporting Staff

Tradesman	(E)	1
Tradesman	(C)	1
Stenographer	(Jr)	1

Ceramics Section

Dr. S.V.K. Rao, SO (SF)
Head, Ceramics Section

Ceramic Fuels and Special Ceramics

Dr. B.D. Zope	(SE)
Dr. Ashok Mohan	(SD)
N.C. Soni	(SD)
Dr. N.S. Anandan	(SD)
R. Bhat	(SD)
P.K. Agnihotri	(SC)
P.V. George	SA(B)
Ram Prasad	(SE)
S.N. Sharma	(SC)

Characterisation and sintering of UO_2, ThO_2, BeO and UC.

Development of UO_2 and UO_2-ZrO_2 plate-type Fuels.

Development of sintered SiC as temperature monitors in irradiation experiments.

Development and fabrication of alumina components for electrical applications and ceramic fabrication.

Capacitor and ferrite ceramics. Development and evaluation of $BaTiO_3$, Ni-Zn-Ferrite bodies and allied systems.

Oxide Ceramics

S.K. Roy	(SE)
B.R. Vyas	(SD)
C.M. Pathak	(SD)
G.E. Prasad	(SD)
G.T. Kamath	(SC)
S. Ramanathan	(C)

Development of ceramic materials for MHD. High temperature oxide ceramics as Al_2O_3, MgO for insulation and rare-earth oxide stabilised ZrO_2 for electrodes.

Development of Al_2O_3 catalyst carriers.

Mechanisms of sintering and metallographic studies.

Development of ceramic oxide solid electrolytes.

Refractory Systems

Dr. A.K. Kulkarni	(SF)
Pranab Das	(SD)
D.D. Upadhyaya	(SD)
P.Y. Dalvi	SA(C)
V.K.S. Nair	SA(B)

Refractory systems. R&D on refractory bodies as mullite, zircon, zirconia and pyrophyllite and steatite systems and high alumina substrates.

SUPPORTING AND ADMINISTRATIVE STAFF

M.G. Joshi	A/Foreman	P.D. Wadawale	T/D
T.S. Shende	T/E	V.G. Kakhandaki	T/D
H.G. Barde	T/E	Smt.L.K Santhappan	Steno (Sr.)
		K.B. Yadav	Helper A